52241|B

E. Balby

ELEMENTS OF CHEMISTRY.

London :
Printed by S. & J. Bentley, Wilson, and Fley,
Bangor House, Shoe Lane.

ELEMENTS OF CHEMISTRY,

INCLUDING THE

ACTUAL STATE AND PREVALENT DOCTRINES OF THE SCIENCE.

BY THE LATE

EDWARD TURNER, M.D. F.R.S. L. & E.

SEVENTH EDITION.

EDITED BY

JUSTUS LIEBIG, M.D. PH.D. F.R.S. L. & E.

PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF GIESSEN;

AND

WILLIAM GREGORY, M.D. F.R.S.E.

PROFESSOR OF CHEMISTRY, KING'S COLLEGE, ABERDEEN.

LONDON:
PRINTED FOR TAYLOR AND WALTON,
UPPER GOWER STREET;
AND SOLD BY MACLACHLAN AND STEWART, EDINBURGH.
M.DCCC.XLII.

95400

WELLCOME
HISTORICAL
MEDICAL
LIBRARY

PREFACE.

In offering to the British Public the Seventh Edition of Professor Turner's Elements of Chemistry, the Editor feels it quite unnecessary to advance anything in recommendation of a work so firmly established in the public favour. The death of its lamented Author has thrown into other hands the task of rendering the Elements of Chemistry equal to the demands made upon such a treatise by the rapid and unceasing progress of discovery,—of giving, in short, to the student, a compendious view of the actual state and prospects of the science.

When the Sixth Edition was projected, in the life-time of the Author, it was arranged that Professor Liebig should undertake the department of Organic Chemistry, while Dr. Turner himself was to re-write the Inorganic Chemistry, that being the department with which he was more especially familiar. The choice of Professor Liebig has been ratified by the unanimous voice of European chemists, by whom he is admitted to be the first living authority in Organic Chemistry.

The delay which has occurred in the completion of that edition, which is finished along with the present, has been chiefly owing to the wish of Professor Liebig to render it what it professes to be,—namely, a durable record of well-established facts. Many laborious series of experiments have been completed in his laboratory with this object alone in view, the results of which are embodied in both editions. This will thus constitute the first tolerably complete account of Organic Chemistry in the English language. In both will be found the latest and most accurate information, as far as it had come into the hands of the English Editor when the respective sheets were written or revised. For examples of the great additional value thus given to the work, the reader is referred to the sections on alcohol and the ethers, on sugar, on benzule, on the vegetable acids; on the oily acids, fixed oils, soaps, and plasters; on the colouring matters and vegetable bases; and, finally, on the azotised products common to the animal and vegetable kingdoms.

Much yet remains to be done, before the boundless field of Organic Chemistry shall be thoroughly explored; but the Editor ventures to entertain the hope that the present work, by making the rising generation of British chemists aware of what their brethren on the Continent have done in this department, may contribute to induce them to cultivate Organic Chemistry, and thus secure for their country a share of the honour of those discoveries which will infallibly be made in this division of their science. So rich, indeed, is the vein of discovery in this mine of research, too long neglected among us, that, in the words of Professor Liebig, "we have only to stoop down in order to pick up discoveries from the ground." It need hardly be added, that, to succeed in this, we must proceed on the only true method, the Baconian, that is, rigid induction from facts accurately observed.

The bulk of that part of the work devoted to Organic Chemistry has been of necessity so much increased, that in the present edition the Editor has been compelled, however reluctantly, to curtail very considerably the sections on heat, light, electricity, and galvanism, which come more properly, in many of their details, into the province of physics than into that of chemistry; the Editor trusts, however, that these subjects will be found as fully treated as is consistent with the character of an elementary work on chemistry.

In the Inorganic Chemistry no material change has been made, except that recently-ascertained facts have been added. The Editor felt that he could not hope to add anything to the beauty and perspicuity of Dr. Turner's exposition of the doctrines of chemistry, and particularly of combination in definite proportions, and of the atomic theory.

One addition has appeared to the Editor indispensable: namely, a sketch of the new views of the constitution of Acids and Salts which at present occupy the attention of chemists. It is yet too early to adopt these views as a principle of arrangement, but the student has a right to expect some account of them. This will be found in the general section on Salts, and also under the head, "Theory of Organic Acids." Some remarks on the same subject will also be found under Phosphoric Acid and its modifications. In the opinion of the Editor, the progress of discovery decidedly tends to establish the principal points of the new doctrine:

namely, that all acids are composed of radicals, simple or compound, united to hydrogen; that, in salts, metals are substituted for this hydrogen; and, lastly, that there exists a class of acids, to which the term *polybasic* may be applied, which require, to form neutral salts, two, three, or more equivalents of base. On this last point, especially, a keen controversy, conducted with consummate talent and praiseworthy moderation on both sides, has been for some time carried on between Dumas and Liebig, the chief advocates of the new views, on the one hand, and Berzelius, the champion of the longer-established doctrine, on the other. As in the case of all scientific controversies, properly conducted, the difference of opinion has led to new researches, the results of which have been highly beneficial to the progress of chemistry.

The whole of the Organic Chemistry has been re-written and new-modeled, and includes not only the facts most recently ascertained, but also a sketch of those views, both in Vegetable and Animal Chemistry, which have lately been developed by Professor Liebig, and which have excited so great an interest.

In reference to the subject of symbols and formulæ, the Editor, in compliance with the method followed in the Sixth Edition, has adopted the simple and highly-useful system recommended by Liebig and Poggendorff. This system is, in his opinion, nearly faultless as a means of condensing the representation of chemical combinations and decompositions into a small space. Its rules are few and easy; and, above all, it is almost universally adopted on the Continent. The Editor has reduced all the formulæ in the work to one system, several having inadvertently been given according to another in the Sixth Edition. All the systems in use, however, are explained, so that the student need have no difficulty in reading any work in which they occur. He would most earnestly recommend to the student, early to familiarize himself with the use of symbols and formulæ. The time has now gone by when their utility could be doubted or denied; indeed, it is not too much to say, that the use of formulæ, by facilitating the comprehension of complicated changes, has materially contributed to the progress of chemical discovery. Symbols and formulæ, however, are not to be considered as an attempt to apply mathematics to chemistry; they are simply abbreviations, and, algebraically considered, they include only the use of + and −, in other words, addition and subtraction.

It has not been considered expedient to make any change in the atomic weights usually adopted in England. Unanimity on this point is no doubt highly desirable among chemists of all nations; but the change ought to proceed from some general congress of chemists, and should not be attempted by individuals. The student should bear in mind, in reading foreign works, that the atomic weights of hydrogen, chlorine, bromine, iodine, cyanogen and nitrogen, adopted on the Continent, are only half as high as those used in England; so that, for example, water, with us, is represented by HO, while, in France and Germany, it is H_2O; chloride of potassium, which in England is KCl, on the Continent is KCl_2; and so on.

Finally, the Editor has to apologise for the errors and imperfections of the work. Those who are best acquainted with the rapid and incessant progress of the science, will be most ready to excuse them; and those who best know its extent, will best appreciate the difficulties which must attend any attempt to compress into one volume, however large, an accurate or practically useful account of Modern Chemistry.

WILLIAM GREGORY.

King's College, Aberdeen,
October 20th, 1842.

CONTENTS.

Page
INTRODUCTION 1

PART I.

IMPONDERABLE SUBSTANCES.

SECT. I. Heat 9
Communication of Heat 10
Radiation 14
On the Cooling of Bodies 22
Effects of Heat . . . . . ib.
Expansion 24
Thermometer 29
Specific Heat 34
Liquefaction 39
Vaporization 44
Ebullition 46
Evaporation 49
Constitution of Gases with respect to Heat . . 56
Sources of Heat 58
SECT. II. Light . . . . . . ib.
SECT. III. Electricity 75
SECT. IV. Galvanism 93

PART II.

INORGANIC CHEMISTRY . . . 133

SECT. I. Affinity 139
On the changes that accompany Chemical Action . 143
On the Circumstances that modify and influence the operation of Affinity 146
On the Measure of Affinity 154
SECT. II. On the Proportions in which Bodies unite, and on the Laws of Combination 155
On the Atomic Theory of Dalton 167
On the Theory of Volumes 171

Page
Table of Equivalent Weights and Volumes . . 173
Chemical Symbols 178
Isomeric Bodies 183
Sect. III. Oxygen 184
Theory of Combustion 188
Sect. IV. Hydrogen.—Water 192
Binoxide of Hydrogen 200
Sect. V. Nitrogen 203
On the Atmosphere 205
Compounds of Nitrogen and Oxygen.—Protoxide . 215
Binoxide of Nitrogen 218
Hyponitrous Acid 222
Nitrous Acid 224
Nitric Acid 226
Sect. VI. Carbon 231
Carbonic Acid 235
Carbonic Oxide 239
Sect. VII. Sulphur 241
Compounds of Sulphur and Oxygen.—Sulphurous Acid . 244
Sulphuric Acid 245
Hyposulphurous Acid 249
Hyposulphuric Acid 250
Sect. VIII. Phosphorus 252
Hypophosphorous Acid 255
Phosphorous Acid 256
Phosphoric Acid 257
Pyrophosphoric Acid 259
Metaphosphoric Acid 260
Sect. IX. Boron.—Boracic Acid 261
Sect. X. Silicon 264
Sect. XI. Selenium 267
Oxide of Selenium, and Selenious and Selenic Acids . 268
Sect. XII. Chlorine 271
Hydrochloric Acid 276
Compounds of Chlorine and Oxygen . . . 281
Chloric and Perchloric Acids . . . 285
Chloride of Nitrogen 287
Chlorides of Carbon 289
Chloride of Sulphur 290
Chlorides of Phosphorus . . . 291
Chloro-carbonic Acid 292
Terchloride of Silicon 293
Chloride of Boron, and Chloro-nitrous Gas . . *ib.*
Nature of Chlorine 295
Sect. XIII. Iodine 297
Hydriodic Acid . . . 301
Oxide of Iodine, Iodous and Iodic Acids . . 303
Periodic Acid 305
Chlorides of Iodine 306

		PAGE
	Iodide of Nitrogen, &c.	307
SECT. XIV.	Bromine	308
	Hydrobromic Acid	311
	Bromic Acid	313
	Chloride of Bromine	314
	Bromide of Sulphur and Phosphorus	315
	Terbromide of Silicon	316
SECT. XV.	Fluorine	*ib.*
	Hydrofluoric Acid	317
	Fluoboric Acid	320
	Fluosilicic Acid	322

ON THE COMPOUNDS OF THE SIMPLE NON-METALLIC ACIDIFIABLE COMBUSTIBLES WITH EACH OTHER.

SECT. I.	Hydrogen and Nitrogen.—Ammonia	324
SECT. II.	Hydrogen with Carbon.—Light carburetted Hydrogen	328
SECT. III.	Compounds of Hydrogen and Sulphur.—Hydrosulphuric Acid	333
	Persulphuretted Hydrogen	336
SECT. IV.	Hydrogen and Selenium.—Hydroselenic Acid	338
SECT. V.	Hydrogen and Phosphorus	339
SECT. VI.	Nitrogen and Carbon.—Cyanogen	344
	Mellon	346
SECT. VII.	Compounds of Phosphorus and Nitrogen	*ib.*
SECT. VIII.	Compounds of Sulphur with Carbon	347
	Compounds of Sulphur with Phosphorus	348
	Compounds of Selenium with Sulphur and Phosphorus Compounds of Selenium with Nitrogen	349

METALS.

	General properties of Metals	351
SECT. I.	Potassium and its Compounds with Oxygen, Chlorine, Sulphur, &c.	371
SECT. II.	Sodium and its Oxides, Chloride, &c.	382
SECT. III.	Lithium and its Oxides, &c.	386
SECT. IV.	Barium and its Oxides, &c.	388
SECT. V.	Strontium, and its Oxide, Chloride, Sulphuret, &c.	392
SECT. VI.	Calcium and its Oxides, Chloride, &c.	394
SECT. VII.	Magnesium and its Oxide, &c.	399
SECT. VIII.	Aluminium.—Alumina	401
SECT. IX.	Glucinium, Yttrium, Thorium, Zirconium, and their Oxides	407
SECT. X.	Manganese, and its Compounds with Oxygen, Chlorine, &c.	414
SECT. XI.	Iron, and its Compounds with Oxygen, Chlorine, Sulphur, &c.	424
	Carburets of Iron.—Steel, Cast Iron, Graphite	435
SECT. XII.	Zinc, and its Compounds with Oxygen, Chlorine, Sulphur, &c.	437
	Cadmium and its Oxide	440
SECT. XIII.	Tin, and its Compounds with Oxygen, Chlorine, &c.	442

		PAGE
SECT. XIV.	Cobalt, Nickel	448
SECT. XV.	Arsenic, and its Compounds with Oxygen, Chlorine, &c.	455
	Tests for Arsenious Acid	458
SECT. XVI.	Chromium, and its Compounds with Oxygen	467
	Sesquichloride of Chromium	472
	Compounds of Chromium with Fluorine, &c.	473
	Vanadium, and its Compounds with Oxygen	475
	Compounds of Vanadium with Chlorine, &c.	482
SECT. XVII.	Molybdenum and its Compounds with Oxygen	483
	Tungsten and its Compounds with Oxygen	487
	Columbium and its Compounds with Oxygen	490
SECT. XVIII.	Antimony, its Oxides, Chlorides, and Sulphurets	493
SECT. XIX.	Uranium and its Oxides	501
	Cerium and its Oxides.—Lantanium	503
SECT. XX.	Bismuth, and its Compounds with Oxygen, Chlorine, and Sulphur	504
	Titanium and its Compounds with Oxygen	506
	Tellurium and its Oxides	510
SECT. XXI.	Copper, and its Compounds with Oxygen, Chlorine, &c.	513
SECT. XXII.	Lead and its Oxides, &c.	519
SECT. XXIII.	Mercury and its Oxides	524
	Chlorides.—Calomel and Corrosive Sublimate	528
	Iodides, Cyanurets, and Sulphurets	531
SECT. XXIV.	Silver, its Oxide, Chloride, &c.	533
SECT. XXV.	Gold, and its Compounds with Oxygen, Chlorine, and Sulphur	538
SECT. XXVI.	Platinum, and its Compounds with Oxygen, &c.	544
SECT. XXVII.	Palladium, Rhodium, Osmium, and Iridium	549
SECT. XXVIII.	On Metallic Combinations.—Alloys	558

SALTS.

	GENERAL REMARKS ON SALTS.—CRYSTALLIZATION	566
SECT. I.	Crystallization	580
	Oxy-salts	596
	Sulphates	598
	Double Sulphates	609
	Sulphites	614
	Hyposulphites and Hyposulphates	*ib.*
	Nitrates	*ib.*
	Nitrites	621
	Chlorates	*ib.*
	Chlorites	623
	Iodates	625
	Phosphates	627
	Pyrophosphates	633
	Metaphosphates	635
	Arseniates	*ib.*

PAGE
Arsenites 638
Chromates 639
Borates 642
Carbonates 643
SECT. II. Hydro-salts 653
Ammoniacal Salts 654
Phosphuretted Hydrogen Salts . . . 657
SECT. III. Sulphur-salts . . . . . ib.
Hydro-sulphurets 658
Carbo-sulphurets 660
Arsenio-sulphurets 661
Molybdo-sulphurets 665
Antimonio-sulphurets 666
Tungsto-sulphurets . . . . . ib.
SECT. IV. Haloid-salts 667
Hydrargo-chlorides . . . . . ib.
Auro-chlorides 668
Platino-chlorides 669
Palladio-chlorides 670
Rhodio-chlorides 671
Iridio-chlorides, and Osmio-chlorides . . ib.
Oxy-chlorides 672
Chlorides with Ammonia 674
Chlorides with Phosphuretted Hydrogen . . 675
Double Iodides 676
Double Bromides and Fluorides . . . 677
Boro-fluorides 678
Silico-fluorides 679
Titano-fluorides 680
Oxy-fluorides 681

PART III.

ORGANIC CHEMISTRY.

Compound Radicals 682
Organic Acids 686
Amide and its Combinations 693
Carbonic Oxide 697
Oxalic Acid and Oxalates 698
Oxamide 705
Rhodizonic Acid 706
Cyanogen 709
Cyanic Acid . . . . . . ib.
Cyanates 710
Fulminic Acid 714
Fulminates . . . . . . ib.
Cyanuric Acid 717

	Page
Hydrocyanic Acid, Prussic Acid	720
Metallic cyanides	724
Hydro-ferro-cyanic Acid	731
Ferro-cyanides	*ib.*
Ferrid-cyanogen	738
Hydro-ferrid-cyanic Acid	739
Ferrid-cyanides	*ib.*
Cobalto-cyanides	740
Hydro-cobalto-cyanic Acid	741
Constitution of Ferro-cyanides	742
Chloride of Cyanogen	743
Bromide of Cyanogen	744
Iodide of Cyanogen	745
Cyanogen and Sulphur	*ib.*
Hydro-sulpho-cyanic Acid	746
Sulpho-cyanide of Ammonium	*ib.*
Metallic Sulpho-cyanides	747
Products of the Decomposition of Cyanogen and its Compounds	749
Products of the Decomposition of Sulpho-cyanogen	750
Mellon and its Compounds	751
Cyanilic Acid	752
Mellon and Potassa	*ib.*
Hydro-persulpho-cyanic Acid	753
Melam and its Products	*ib.*
Composition of Melamine, Amiline, and Ammelide	757
Cyanogen and Hydro-sulphuric Acid	*ib.*
Uric Acid	759
Urates of Potassa and Soda	761
Allantoine.—Alloxan	*ib.*
Alloxanic Acid	764
Alloxanates	765
Mesoxalic, Mykomelinic, Parabanic, and Oxaluric Acids	*ib.*
Thionuric Acid	769
Uramile, Uramilic Acid, and Salts	772
Alloxantine, Murexide, Murexan	*ib.*
Appendix to Compounds of Uric Acid	778
Benzule and Table of its Compounds	779
Theoretical views of the connexion of the Compounds of Benzule	807
Salicule, Saliculous Acid, and Compounds, &c.	808
Salicine, Saliretine, Chlorosalicine, Phloridzine	816
Phloretine, Phloridzeine, Cinnamule	819
Oil of Cinnamon or Cassia, Cinnamic Acid	821
Salts of Cinnamic Acid, &c.	822
Oil of Balsam of Peru	823
Ethule, Ether, Alcohol, and Compounds	825
Double Salts of Oxide of Ethule	844
Oxide of Ethule and Phosphoric Acid	846
Salts of Oxide of Ethule	848
Double Salts of Oxalic Acid with Oxide of Methule and Metallic Oxides	853

PAGE
Xanthic Acid 855
Double Salts of Bisulphuret of Carbon with Oxide of Ethule and Metallic Oxides . . . . . . ib.
Compounds of Ethule of uncertain constitution . . . 858
Transformations and Products of the Decomposition of Ethule and its Compounds 859
Ethionic and Isethionic Acids 863
Acetule and its Compounds with Oxygen . . . 867
Aldehyde, Acetal 869
Transformation of Aldehyde 871
Acetylic and Acetic Acids 874
Acetic Acid and Bases 879
Products of the Decomposition of Ether and its Compounds by Chlorine . 887
Chloral, Chloracetic Acid 889
Heavy Muriatic Ether, Bromal 893
Iodine and Alcohol 894
Products of Alcohol, the constitution of which is uncertain . . 895
Products of Acetic Acid, and the Acetates . . . 900
Action of Chlorine and Iodine on Acetone and Mesitylene . . 905
Compounds containing Arsenic derived from Acetule . . 906
Constitution of Ether and its Compounds 911
Cane Sugar, Combination with Bases 914
Grape Sugar, with Bases 919
Sulpho-saccharic Acid 926
Products of the Decomposition of Cane and Grape Sugar . . ib.
Action of Acids on Sugar 927
Action of Alkalies 929
Action of Heat on Sugar 930
Products of the Oxidation of Sugar 931
Remarks on the constitution of the Compounds of the different kinds of Sugar, and the Products of their Decomposition . . . 933
Sugar of Milk or Lactine 935
Products of Oxidation of Sugar of Milk 937
Salts of Mucic Acid 938
Mushroom Sugar, Tasteless Sugar 942
Alcoholic or Vinous Fermentation 944
Viscous Fermentation 947
Mannite, Lactic Acid, Lactates 948
Methule, Oxide of Methule, &c. 952
Compounds of Methule with negative non-metallic bodies, and with Sulphur 955
Oxygen Salts of Methule 957
Double Salts of the Sulphate of Oxide of Methule . . . 959
Other Compounds of Methule.—Formule . . . 963
Formic Acid, Formates 967
Compounds of Formule with Chlorine, &c. . . . 972
Action of Chlorine on the Compounds of Methule . . . 976
Products of the Distillation of Wood of uncertain constitution . 979
Cetule 980
Amule or Amyle 982

PAGE
Products of the Oxidation of Hydrated Oxide of Amule, and the action of Phosphoric Acid and of Chlorine on the same . . . 985
Glycerule 986
Meconic Acid 989
Meconates, Komenic Acid, Komenates 991
Pyromeconic Acid, Tannic Acid, Tannates 993
Products of the Decomposition of Tannic Acid . . . 994
Gallic Acid, Gallates, Action of Heat on Gallic and Tannic Acids . 996
Pyrogallic Acid, Pyrogallates, Metagallic Acid . . . 997
Nut Galls, Ellagic Acid 999
Compounds similar in their relations to Tannic Acid . . 1000
Catechu, Catechine . . . . . . ib.
Citric Acid, Citrates, Action of Heat on the former . . 1002
Aconitic Acid, Aconitates 1006
Itaconic Acid, Itaconates 1007
Citraconic Acid, Citraconates 1008
Tartaric Acid, Tartrates . . . . . ib.
Action of Heat on Tartaric Acid 1016
Racemic Acid, Malic Acid, Malates 1019
Action of Heat on Malic Acid 1020
Maleic Acid, Fumaric Acid 1021
Acids of unknown constitution 1022
Kinic Acid, Salts of Kinic Acid . . . . ib.
Volatile Acids of Butter 1024
Butyric Acid, Salts of Butyric Acid . . . . ib.
Caproic Acid, Capric Acid 1025
Hircic, Phocenic, and Sabadillic Acids 1026
Crotonic and Camphoric Acids 1027
Camphor and Oil of Camphor 1029
Valerianic Acid, Action of Chlorine on 1030
Œnanthic, Rocellic, and Veratric Acids 1032
Cuminic, Caryophyllic, Cocoic Acids 1033
Sericic, Palmitic, Cetulic, and Margaric Acids . . . 1035
Salts of Margaric Acid 1039
Stearic Acid and Bases 1040
Composition of Stearic and Margaric Acids 1044
Amber, Oleic Acid, Salts of Oleic Acid 1051
Sebacic Acid, Salts of Sebacic Acid 1056
Action of Nitric and Nitrous Acids on Oleic Acid . . . 1057
Elaidic Acid, and Salts of Elaidic Acid . . . . ib.
Action of Alkalies at a high temperature on Oleic and Elaidic Acids . 1062
Acids of Castor Oil, Appendix to the Oily Acids, Natural Fixed Oils and Fats 1063
Action of Heat on Fats, Oil Gas 1065
Action of simple Substances on Fixed Oils 1067
Action of Sulphuric Acid on Fixed Oils 1068
Metoleic and Hydroleic Acids 1071
Action of Nitrous Acid on Oils 1073
Actions of Metallic Oxides on Fixed Oils and Fats . . . 1074
Plasters 1078

Page

Oils and Fats occurring in Nature 1079
Drying Oils, Fish and Train Oil . . . . *ib.*
Liquid Fat Oils, Solid Fat Oils or Fats 1080
Wax, Organic Acids little examined 1085
Volatile Essential Oils 1086
Non-oxygenized Essential Oils 1089
Oxygenated Essential Oils 1093
Essential Oils containing Sulphur 1099
Appendix to Essential Oils 1101
Caoutchouc 1103
Resins, Resinous Varnishes 1105
Products of the Distillation of Common Resin . . . 1110
Non-azotized vegetable colouring matters 1111
Yellow and Red Colouring Matters 1112
Blue and Green ditto 1117
Non-azotized Vegetable principles, the nature of which is not exactly known 1118
Lecanorine, Orcine, Erythrine 1126
Archil, Cudbear, Litmus 1131
Indigo, Composition of Blue and White 1134
Action of Sulphuric Acid on Indigo 1135
Products of the Oxidation of Indigo 1137
Action of Chlorine on Isatine 1138
Products of the action of Chlorine on Indigo . . . 1141
Products of the action of Nitric Acid on Indigo . . . 1143
Products of the action of Alkalies on Indigo . . . 1144
Commercial Indigo 1145
Cochineal-red, Carmine, Kermes 1147
Aloes, action of Nitric Acid on . . . . . *ib.*
Asparagine 1150
Organic Bases or Alkalies 1151
Volatile Bases, Aniline, Nicotine, &c. 1154
Bases from Oil of Mustard, Thiosinnamine, &c. . . . 1156
Bases of Cinchona Bark, Quinine, Cinchonine, &c. . . 1157
Bases of the Papaveraceæ, Morphia, Codeine, &c. . . . 1159
Bases found in the Solanaceæ, Strychnaceæ, and other natural families. Hyoscyamine, Daturine, Stramonine, Atropine, Solanine, Veratrine, Jervine, Sabadilline, Strychnia, Brucine, Delphine, Staphysine, Aconitine, Picrotoxine, Menispermine, Hematine, Harmaline, Piperine, Berberine, Corydaline, Caffeine, &c. 1164
Neutral or indifferent Compounds which occur generally in Vegetables Starch, Dextrine, Diastase, Inuline, Moss or Lichen Starch . 1170
Gum, Gum Tragacanth, Woody Fibre or Lignine . . . 1174
Wood or Brown Coal, Mineral Coal . . . . *ib.*
Products of the action of Heat on Wood and Coal. Eupion, Creosote, Picamar, Capnomor, Pittacal, Cedriret, Paraffine, Naphthaline, &c. . 1177
Indifferent Azotized Substances, common to the Vegetable and Animal Kingdoms. Proteine, and its modifications . . . 1183
Albumen, Fibrine, Caseine 1185
The Blood 1191

Page

Muscular Tissue, Gelatinous Tissue, Gelatine, Chondrine, Arterial Membrane, Horny Matter, Feathers, Pigmentum Nigrum Oculi . . . 1192
Brain and Nervous Matter 1195
Cerebric Acid, Oleophosphoric Acid, Cholesterine . . . 1196
Bones, Teeth 1197
Animal Secretions and Excretions 1198
Milk, Saliva, Gastric Juice, Pancreatic Juice . . . *ib.*
Bile and Biliary Calculi 1200
Choleic Acid, Choloidic Acid, Taurine, Cholic Acid, Biliary Calculi, Lithofellic Acid . . . . . . *ib.*
Excrements, Lymph, Mucus, Pus 1203
Urine, Analysis of. Urine of Herbivora, of Carnivora, of Serpents . . 1205
Urinary Calculi—Urate of Ammonia, Bone Earth, Ammoniaco-magnesian Phosphate, Fusible Calculus, Oxalate of Lime or Mulberry Calculus, Xanthic Oxide, Cystic Oxide . . . . . *ib.*
Changes which occur during the life, growth, and nutrition of Vegetables and Animals 1207

PART IV.

CHEMICAL ANALYSIS . . . 1223

Sect. I. Manipulations in Analytical processes . . 1224
Sect. II. Qualitative Analysis 1227
Sect. III. Quantitative Analysis 1232
Sect. IV. Analysis of Mineral Waters . . . 1237
Composition of Mineral Waters . . . 1243

APPENDIX.

I. Table of Equivalents or Atomic weights of Elements . . 1247
II. Table of the elastic force of Aqueous vapour . . 1248
III. Table of the elastic force of the vapour of Alcohol, &c. . . 1250
IV. Table for the conversion of degrees on the Centigrade Thermometer into degrees of Fahrenheit's Scale 1251
V. Table of the strength of Sulphuric Acid . . . 1253
VI. Table of the strength of Nitric Acid 1254
VII. Table of the strength of Alcohol 1255
VIII. Table of Specific Gravities indicated by Baumé's Hydrometer . *ib.*
General Index 1256

Errata.

Page 391, line 18, *for* "fluor" *read* "flour."
539, line 17, *for* "attached" *read* "attacked."

INTRODUCTION.

Material substances are endowed with two kinds of properties, physical and chemical; and the study of the phenomena occasioned by them has given rise to two corresponding branches of knowledge, *Natural Philosophy* and *Chemistry*.

The physical properties are either general or secondary. The general are so called because they are common to all bodies; the secondary, from being observable in some substances only. Among the general may be enumerated extension, impenetrability, mobility, extreme divisibility, gravitation, porosity, and indestructibility.

Extension is the property of occupying a certain portion of space: a substance is said to be *extended* when it possesses length, breadth, and thickness. By *impenetrability* is meant, that no two portions of matter can occupy the same space at the same moment. Every thing that possesses extension and impenetrability is matter.

Matter, though susceptible of *rest and motion*, has no inherent power either of beginning to move when at rest, or of arresting its progress when in motion. Its indifference to either state has been expressed by the term *vis inertiæ*, as if it depended on some peculiar force resident in matter, whereas it arises from matter being absolutely passive, and thereby subject to the influence of every force which is capable of acting upon it.

Matter is *divisible* to an extreme degree of minuteness. A grain of gold may be so extended by hammering that it will cover 50 square inches of surface, and contain two millions of visible points; and the gold which covers the silver wire, used in making gold lace, is spread over a surface twelve times as great. A grain of iron, dissolved in nitro-hydrochloric acid, and mixed with 3137 pints of water, will be diffused through the whole mass: by means of the ferro-cyanuret of potassium, which strikes an uniform blue tint, some portion of iron may be detected in every part of the liquid. The grain of iron is hence inferred to have been divided into rather more than 24 millions of parts; and if the dilution were carried still further, the diffusion of iron through the whole liquid might be proved by concentrating any portion of it by evaporation, and detecting the metal by its appropriate tests.

A keen controversy existed at one time concerning the divisibility of matter, some philosophers affirming it to be infinitely divisible, while others maintained an opposite opinion. Owing to the imperfection of our senses the question cannot be determined by direct experiment, because matter certainly continues to be divisible long after it has ceased to be an object of sense. The decision, if effected at all, can only be accomplished indirectly, as an inference from other phenomena. In favour of the former view it was urged, on mathematical grounds, that a surface admits of division without limit; and that to whatever degree matter is divided, it may still be conceived, in possessing extension and surface, to be susceptible of still further division. Plausible, however, as this mode of reasoning may appear, the opposite opinion is daily becoming more general. It is now commonly believed that matter consists of ultimate particles or molecules, which may indeed be conceived to be divisible, but which by hypothesis are assumed to be infinitely hard and impenetrable, and on that account to be incapable of division. These ultimate particles have received the appellation of *atoms*, (from the privative α and τεμνειν to cut,) as expressive of their nature. The arguments adduced in support of this opinion are principally drawn from the phenomena of chemistry, and from the relations which have been observed to exist between the composition and form of crystallized bodies. These subjects will be considered hereafter: it will now suffice to state, in order to show the nature of the argument, that the supposed existence of atoms accounts for numerous facts, which cannot be satisfactorily explained on any other principle.

All bodies descend in straight lines towards the centre of the earth, when left at liberty at a distance from its surface. The power which produces this effect is termed *gravity*, *attraction of gravitation*, or *terrestrial attraction*; and the force required to separate a body from the surface of the earth, or prevent it from descending towards it, is called its *weight*.. Every particle of matter is equally affected by gravity; and therefore the weight of any body will be proportionate to the number of ponderable particles which it contains.

The minute particles of which bodies consist are disposed in such a manner as to leave certain intervals or spaces between them, and this arrangement is called *porosity.* These interstices may sometimes be seen by the naked eye, and frequently by the aid of glasses; but were they wholly invisible, it would still be certain that they exist. All substances, even the most compact, may be diminished in bulk either by mechanical force or a reduction of temperature. It hence follows that their particles must touch each other at a very few points only, if at all; for if their contact were so perfect as to leave no interstitial spaces, then would it be impossible to diminish the dimensions of a body, because matter is incompressible and cannot yield.—When therefore a body expands, the distance between its particles is increased; and, conversely, when it contracts or diminishes in size, its particles approach each other.

By *indestructibility* is meant, that, according to the present laws of nature, matter never ceases to exist. This statement seems at first view contrary to fact. Water and volatile substances are dissipated by heat, and lost; coals and wood are consumed in the fire, and disappear. But in these and all similar phenomena not a particle of matter is annihilated. The apparent destruction is owing merely to a change of form or composition; for the same material particles, after having undergone any number of such changes, may still be proved to possess the characteristic properties of matter.

The *secondary* properties of matter are opacity, transparency, softness, hardness, elasticity, colour, density, solidity, fluidity, and others of a like nature. Several of these properties, especially those last specified, depend on the relative intensity of two opposite forces—cohesion and repulsion. It is inferred, from the divisibility of matter, that the substance of solids and liquids is made up of an infinity of minute particles adhering together so as to constitute larger masses; and that the mutual adhesion of these particles is owing to a power of reciprocal attraction. This force is called *cohesion*, *cohesive attraction*, or the *attraction of aggregation*, in order to distinguish it from terrestrial attraction. Gravity is exerted between different masses of matter, and acts at sensible and frequently at very great distances; while cohesion exerts its influence only at insensible and infinitely small distances. It enables similar molecules to cohere, and tends to keep them in that condition. It is best exemplified by the force required to separate a hard body, such as iron or marble, into smaller fragments; or by the weight which twine or metallic wire will support without breaking.

The tendency of cohesion is manifestly to bring the ultimate particles of bodies into immediate contact; and such would be the result of its influence, were it not counteracted by an opposing force, a principle of repulsion, which prevents their approximation. It is a general opinion among philosophers, supported by very strong facts, that this repulsion is owing to the agency of heat, which is somehow attached to the elementary molecules of matter, causing them to repel one another. Material substances are therefore subject to the action of two contrary and antagonizing forces, one tending to separate their particles, the other to bring them into closer proximity. The form of bodies, as to solidity and fluidity, is determined by the relative intensity of these powers. Cohesion predominates in solids, in consequence of which their particles are prevented from moving freely on one another. The particles of a fluid, on the contrary, are far less influenced by cohesion, being free to move on each other with very slight friction. Fluids are of two kinds; elastic fluids or aëriform substances, and inelastic fluids or liquids. Cohesion seems wholly wanting in the former; they yield readily to compression, and expand when the pressure is removed; indeed, the space they occupy is chiefly determined by the force which compresses them. The latter, on the contrary, do not yield perceptibly to ordinary degrees of compression, nor does an appreciable dilatation ensue from the removal of pressure, the tendency of repulsion being in them counterbalanced by cohesion.

Matter is subject to another kind of attraction different from those yet mentioned, termed *chemical attraction* or *affinity*. Like cohesion it acts only at insensible distances, and thus differs entirely from gravity. It is distinguished from cohesion by being exerted between dissimilar particles only, while the attraction of cohesion unites similar particles. Thus, a piece of marble is an aggregate of smaller portions attached to each other by cohesion, and the parts so attached are called *integrant* particles; each of which, however minute, being as perfect marble as the mass itself. But the integrant particles consist of two substances, lime and carbonic acid, which are different from one another as well as from marble, and are united by chemical attraction. They are the *component* or *constituent* parts of marble. The integrant particles of a body are therefore aggregated together by cohesion; the component parts are united by affinity.

The chemical properties of bodies are owing to affinity, and every chemical phenomenon is produced by the operation of this principle. Though it extends its influence over all substances, yet it affects them in very different degrees, and is subject to peculiar modifications. Of three bodies, A, B, and C, it is often found that B and C evince no affinity for one another, and therefore do not combine; that A, on the contrary, has an affinity for B and C, and can enter into separate combination with each of them; but that A has a greater attraction for C than for B, so that if we bring C in contact with a compound of A and B, A will quit B and unite by preference with C. The union of two substances is called *combination;* and its result is the formation of a new body endowed with properties peculiar to itself, and different from those of its constituents. The change is frequently attended by the destruction of a previously existing compound, and in that case *decomposition* is said to be effected.

The operation of chemical attraction, as thus explained, lays open a wide and interesting field of inquiry. One may study, for example, the affinity existing between different substances; an attempt may be made to discover the proportions in which they unite; and finally, after collecting and arranging an extensive series of insulated facts, general conclusions may be deduced from them. Hence chemistry may be defined the science, the object of which is to examine the relations that affinity establishes between bodies, ascertain with precision the nature and constitution of the compounds it produces, and determine the laws by which its action is regulated.

Material substances are divided by the chemist into simple and compound. He regards those bodies as compound, which may be resolved into two or more kinds of ponderable matter; those as simple or elementary, which contain but one. The number of the latter amounts only to fifty-four; and of these, agreeably to our present knowledge, all the bodies in the earth consist. The list, a few years ago, was somewhat different from what it is at present; for the acquisition of improved methods of analysis has enabled chemists to demonstrate that some substances, which were once supposed to be simple, are in reality compound; and it is probable that a similar fate awaits some of those which are at present regarded as simple.

The composition of a body may be determined in two ways, analytically or synthetically. By analysis, the elements of a compound are separated from one another, as when water is resolved by the agency of galvanism into oxygen and hydrogen; by synthesis they are made to combine, as when oxygen and hydrogen unite by the electric spark, and generate a portion of water. Each of these kinds of proof is satisfactory; but when they are conjoined—when water is resolved into its elements, and then reproduced by their union—the evidence is in the highest degree conclusive.

I have followed, in the composition of this treatise, the same general arrangement which I adopt in my lectures. It is divided into four principal parts. The first comprehends an account of the nature and properties of *Heat*, *Light*, and *Electricity*,—agents so diffusive and subtile, that the common attributes of matter cannot be perceived in them. They are altogether destitute of weight; at least, if they possess any, it cannot be discovered by our most delicate balances, and hence they have received the appellation of *Imponderables.* They cannot be confined and exhibited in a mass like ordinary bodies; they can be collected only through the intervention of other substances. Their title to be considered material is therefore questionable, and the effects produced by them have accordingly been attributed by some to certain motions or affections of common matter. It must be admitted, however, that they appear to be subject to the same powers that act on matter in general, and that some of the laws which have been determined concerning them, are exactly such as might have been anticipated on the supposition of their materiality. It hence follows, that we need only regard them as subtile species of matter, in order that the phenomena to which they give rise may be explained in the language, and according to the principles, which are applied to material substances in general; and I shall therefore consider them as such in my subsequent remarks.

The second part comprises *Inorganic Chemistry.* It includes the doctrine of affinity, and the laws of combination, together with the chemical history of all the elementary principles hitherto discovered, and of those compound bodies which are not the product of organization. Elementary bodies are divided into the non-metallic and metallic; and the substances contained in each division are treated in the order which, it is conceived, will be most convenient for the purposes of teaching. From the important part which oxygen plays in the economy of nature, it is necessary to begin with the description of that principle; and from the tendency it has to unite with other bodies, as well as the importance of the compounds it forms with them, it will be useful, in studying the history of each elementary body, to describe the combinations into which it enters with oxygen gas. The remaining compounds which the non-metallic substances form with each other will next be considered. The description of the individual metals will be accompanied by a history of their combinations, first with the simple non-metallic bodies, and afterwards with each other. The last division of this part will comprise a history of the salts.

The third general division of the work is *Organic Chemistry*, a subject which will be conveniently discussed under two heads, the one comprehending the Chemistry of the compound Radicals, the other treating of the influence of Life on Chemical Products.

The fourth part contains brief directions for the performance of *Analysis*.

ELEMENTS

OF

CHEMISTRY.

PART I.

IMPONDERABLE SUBSTANCES.

SECTION I.

HEAT, OR CALORIC.

The term *Heat*, in common language, has two meanings: in the one case, it implies the sensation experienced on touching a hot body; in the other, it expresses the cause of that sensation. When used in the latter sense, it is synonymous with the word *Caloric* (from *Calor*, heat), which is employed exclusively to signify the cause or agent by which all the effects of heat are produced.

Heat, on the supposition of its being material, is a subtile fluid, the particles of which repel each other, and are attracted by all other substances. It is imponderable; that is, it is so exceedingly light, that a body undergoes no appreciable change of weight, either by the addition or abstraction of heat. It is present in all bodies, and cannot be wholly separated from them; for if a substance, however cold, be transferred into an atmosphere which is still colder, a thermometer placed in the body will indicate the escape of heat. That its particles repel one another, is proved by observing that it flies off from a heated body; and that it is attracted by other substances, is inferred from the tendency it has to penetrate their particles, and to be retained by them.

Heat may be transferred from one body to another. Thus, if a cup of mercury at 60° be plunged into hot water, heat passes rapidly from one into the other, until the temperature in both is the same; that is, till a thermometer placed in each stands at the same height. All bodies on the earth are constantly tending to attain an equality, or what is technically called an *equilibrium*, of temperature. If, for example, a number of substances of different temperature be enclosed in an apartment, in which there is no actual source of heat, they will very soon acquire an equilibrium, so that a thermometer will stand at the same point in all. Our varying sensations of heat and cold are owing to a like cause. On touching a hot body, heat passes from it into the hand, and excites the feeling of warmth; when we touch a cold body, heat is communicated to it from the hand, and thus arises the sensation of cold.

Heat is communicated from a hot body to others which are colder in two ways, by *direct contact*, and by *radiation*. By *direct contact*, when the hot body touches a cold one, so that the heat may pass directly from one into the other; as when a bar of iron is put into a fire, or the hand plunged into hot water. By *radiation*, when the heat leaps as it were from a hot to a cold body through an appreciable interval; as when a red-hot ball, suspended in the vacuum of an air-pump, distributes its heat to surrounding objects, or when we are warmed by standing at some distance before a fire. In studying these phenomena we must regard both the loss of heat in the hot body, and the gain of heat in the cold one. The mode in which a hot body cools is, firstly, by giving off heat from its surface either by contact or radiation, or both conjointly; and secondly, by the heat in its interior passing from particle to particle through its substance to its surface. The heating of a cold body is effected, firstly, by heat passing into its surface either by contact or radiation, or by both conjointly; and, secondly, by the heat at its surface passing from particle to particle through its interior portions. Hence, in tracing the laws which regulate the distribution of heat, we shall successively consider the communication of heat from one body to another by *contact*, its passage from particle to particle of the same substance or the *conduction* of heat, and its transfer from a sensible distance or *radiation*.

COMMUNICATION OF HEAT BY CONTACT.

The principal conditions which influence the communication of heat from one body to another by contact, are the degree of contiguity, and the conducting power of the substances. The more perfect the approximation, the more rapid, *cæteris paribus*, is the transfer. The contact of two solids, or of a solid with a gas, is in general of a less perfect kind, and at fewer points, than that between a solid and a liquid; and hence, so far as *contact alone* is concerned, the transfer is more rapid in the latter case than in the former. It is still more rapid when liquids are mixed with each other, or gases with gases, owing to the intermixture of their particles. When bodies touch each other at their surfaces only, the question becomes one of conduction, the rapidity of transfer depending on the velocity with which heat passes through the substances in contact. Thus, if a hot mass of iron and another of marble, of equal size, form, and temperature, be plunged into equal quantities of cold water, the iron will cool faster than the marble, because heat passes more rapidly through the substance of the former than through that of the latter. Were two pieces of hot iron similarly plunged, one into mercury, and the other into water, the piece in contact with mercury would cool most rapidly, because that metal is a better conductor than water. Were the experiment made by immersing the iron into mercury, and the marble into water, the rapidity of cooling in the former would very much exceed that in the latter, from two causes;—both from heat passing more rapidly through iron than through marble, and from its being conveyed away more rapidly by mercury than by water. The same principle explains the unequal sensation caused by bodies of equal temperature. Thus the hand receives a more vivid impression of warmth by touching hot iron than from glass of the same temperature; because the quantity of heat which in a given time can be brought from the interior to the surface of the hot body, so as to pass into the skin, is much greater in iron than in glass. In like manner, cold iron feels colder than glass of the same temperature, because the former conveys away from the skin more heat in a given time than the glass.

CONDUCTION OF HEAT.

By this term is expressed the passage of heat from particle to particle through the substance of bodies. Heat is said to be conducted by them or to pass by *conduction*, and the property on which its transmission depends is termed *conducting power*.

Heat obviously passes through bodies with different degrees of velocity. Some substances oppose very little impediment to its passage, while it is transmitted slowly by others. One cannot leave one end of a rod of iron for some time in the fire, and then touch its other extremity, without danger of being burned, though this may be done with perfect safety with a rod of glass or of wood. The observation of these and similar facts, has led to the division of bodies into *conductors* and *non-conductors* of heat. The former division, of course, includes those bodies, such as the metals, which allow heat to pass freely through their substance; and the latter comprises those which do not give an easy passage to it, such as stones, glass, wood, and charcoal.

Some experiments have been made by Despretz, apparently with great care, on the relative conducting power of the metals and some other substances, and the results are contained in the following table. (An. de Ch. et Ph. xxxvi. 422.)

Gold	1000	Tin	303·9
Silver	973	Lead	179·6
Copper	898·2	Marble	23·6
Platinum	381	Porcelain	12·2
Iron	374·3	Fine clay	11·4
Zinc	363		

An ingenious plan was adopted by Count Rumford (Phil. Trans. 1792,) for ascertaining the relative conducting power of the different materials employed for clothing. He enveloped a thermometer in a glass cylinder blown into a ball at its extremity, and filled the interstices with the substance to be examined. Having heated the apparatus to the same temperature in every instance by immersion in boiling water, he transferred it into melting ice, and observed carefully the number of seconds which elapsed during the passage of the thermometer through 135 degrees. When there was air between the thermometer and cylinder, the cooling took place in 576 seconds; when the interstices were filled with fine lint, it took place in 1032″; with cotton wool in 1046″; with sheep's wool in 1118″; with raw silk in 1284″; with beaver's fur in 1296″; with eider down in 1305″; and with hare's fur in 1315″. The general practice of mankind is therefore fully justified by experiment. In winter, clothing of silk or wool is used in order to retain the animal heat; while in summer, cotton or linen stuffs are preferred, that the heat of the body may the more easily escape.

The conducting power of solid bodies does not seem to be related to any of the other properties of matter; but it approaches nearer to the ratio of their densities than to that of any other property.

Liquids may be said, in one sense, to have the power of conveying heat with great rapidity, though in reality they are very imperfect conductors. This peculiarity is referable to the mobility which subsists among the particles of all fluids, and to the change of size which is invariably produced by a change of temperature. When any particles of a liquid are heated they expand, thereby becoming specifically lighter than those which have not received an increase of temperature; and if the former happen to be covered by a stratum of the latter, these from their greater density will descend, while the warmer and lighter particles will be pressed upwards. If, therefore, heat enter at the bottom of a vessel containing a liquid, a double set of currents must be immediately established, the one of hot particles rising towards the surface, and the other of colder particles descending to the bottom. These currents take place with such rapidity, that if a thermometer be placed at the bottom, and another at the top of a long jar, the fire being applied below, the upper one will begin to rise almost as soon as the lower. The transport of hot particles by this process has been termed the *convection* of heat.

But if, instead of heating the bottom of the jar, the heat enter by the upper surface, very different phenomena will be observed. The intestine movements cannot then be formed, because the heated particles, from being lighter than those below them, remain constantly at the top: the heat can descend through the fluid only by transmission from particle to particle, a process which takes place so very tardily, as to have induced Count Rumford to deny that water can conduct at all. In this, however, he was mistaken; for the opposite opinion has been successfully supported by Hope, Thomson, and the late Dr. Murray, though they all admit that water, and liquids in general, mercury excepted, possess the power of conducting heat in a very slight degree.

It is extremely difficult to estimate the conducting power of aëriform fluids. Their particles move so freely on each other, that the moment a particle is dilated by heat, it is pressed upwards with great velocity by the descent of colder and heavier particles, so that an ascending and descending current is instantly established. Besides, gaseous bodies allow a passage through them by radiation. Now the quantity of heat which passes by these two channels is so much greater than that which is conducted from particle to particle, that we possess no means of determining their proportion. It is certain, however, that the conducting power of gaseous fluids is exceedingly imperfect, probably even more so than that of liquids.

RADIATION.

When the hand is placed beneath a hot body suspended in the air, a distinct sensation of warmth is perceived, though from a considerable distance. This effect does not arise from the heat being conveyed by means of a hot current; since all the heated particles have an uniform tendency to rise. Neither, for reasons above assigned, can it depend upon the conducting power of the air; because aërial substances possess that power in a very low degree, while the sensation in the present case is excited almost on the instant. There is yet another mode by which heat passes from one body to another; and as it takes place in all gases, and even *in vacuo*, it is inferred that the presence of a medium is not necessary to its passage. This mode of distribution is called *Radiation* of Heat, and the heat so distributed is called *Radiant* or *Radiated Heat.* It appears, therefore, that a heated body suspended in the air cools, or is reduced to an equilibrium with surrounding bodies, in three ways; first, by the conducting power of the air, the influence of which is very trifling; secondly, by the mobility of the air in contact with it; and thirdly, by radiation.

Laws of Distribution.—Heat is emitted from the surface of a hot body equally in all directions, and in right lines, like radii drawn from the centre to the surface of a sphere; so that a thermometer placed at the same distance on any side would stand at the same point, if the effect of the ascending current of hot air could be averted. The calorific rays, thus distributed, pass freely through a vacuum and the air, without being arrested by the latter or in any way affecting its temperature. When they fall upon the surface of a solid or liquid substance they may be disposed of in three different ways:—1, they may rebound from its surface, or be *reflected;* 2, they may be received into its substance, or be *absorbed;* and, 3, they may pass directly through it, or be *transmitted.* In the first and third cases, the temperature of the body on which the rays fall is altogether unaffected; whereas, in the second, it is increased. The heating influence varies with the distance from the radiating body. The rate or law of decrease, as ascertained by careful experiment, and as may be inferred from mathematical considerations, is, that the intensity of heat, like that of light, diminishes in the same ratio as the squares of the distances from the radiating point increase. Thus the thermometer will indicate four times less heat at two inches, nine times less at three inches, and sixteen times less at four inches, than it did when it was only one inch from the heated substance.

The radiation of heat by hot bodies is singularly influenced by the nature and condition of their surfaces, a circumstance which was first examined by Leslie, to whose Essay on Heat, published in 1804, we must still refer for most of our knowledge on this subject. It follows from these researches that velocity of radiation depends more on the *surface* than the *substance* of a radiating body:—that the most imperfect radiators are to be sought among those bodies which are highly smooth and bright, such as polished gold, silver, tin, and brass; but that these same metals radiate freely when their smoothness and polish are destroyed, as by scratching their surfaces with a file, or covering them with whiting or lamp black. A metallic surface seems adverse to radiation independently of its smoothness, since a highly-polished piece of glass radiates far better than an equally polished metallic surface. Scratching a surface probably favours radiation by multiplying the number of radiating points.

Some interesting experiments have been made by Dr. Stark of Edinburgh, (Phil. Trans. 1833, Part II.) illustrative of the connection between radiation and the colour of surfaces. The bulb of a delicate thermometer was successively surrounded by equal weights of differently coloured wool, was placed in a glass tube, heated by immersion in hot water to 180°, and then cooled to 50° in cold water. The times of cooling were 21 minutes with black wool, 26 with red wool, and 27 with white wool. Concurring results were obtained with flour of different colours. Likewise, black wool was found to collect more dew than an equal weight of white wool, other circumstances being alike.—This is the first time that direct experiments, seemingly unexceptionable, have been made in proof of the influence of colour over radiation.

Reflection of Heat.—The existence of a reflecting power may be shown by standing at the side of a fire in such a position that the heat cannot reach the face directly, and then placing a plate of tinned iron opposite the grate, and at such an inclination as permits the observer to see in it the reflection of the fire: as soon as it is brought to this inclination, a distinct impression of heat will be perceived upon the face. If a line be drawn from a radiating substance to the point of a plane surface by which its rays are reflected, and a second line from that point to the spot where its heating power is exerted, the angles which these lines form with a line perpendicular to the reflecting plane are called the angles of *incidence* and *reflection*, and are invariably equal to each other. It follows from this law, that when a heated body is placed in the focus of a concave parabolic reflector, the diverging rays which strike upon it assume a parallel direction with respect to each other; and that when these parallel rays impinge upon a second concave reflector standing opposite to the former, they are made to converge, so as to meet together in its focus. Their united influence is thus brought to bear upon a single point.

It has been known for ages that the heat contained in the solar rays admits of being reflected by mirrors, and a like property has long since been recognized in the rays emitted by red-hot bodies; but that heat emanates in invisible rays, which are subject to the same laws of reflection as those that are accompanied by light, is a modern discovery, noticed indeed by Lambert, but first decisively established by Saussure and Pictet of Geneva. They first proved it of an iron ball heated so as not to be luminous even in the dark, and then of a vessel of boiling water (Pictet's Essai sur le Feu, p. 65, 1790); but for most of our knowledge of this subject we must again refer to the labours of Leslie. He demonstrated that the reflecting power depends on the nature and condition of surfaces, and that those qualities which are adverse to radiation, are precisely such as promote reflection. Bright smooth metallic surfaces, as polished silver, brass, or tin, which are retentive of their own heat, are little prone to receive heat from other sources, but cause such rays to fly off from them; while those qualities of a surface which facilitate radiation from a hot body, likewise unfit it for reflecting the rays which fall upon it from surrounding objects. His experiments, indeed, justify the conclusion that the faculty of radiation is inversely as that of reflection.

Absorption of Heat.—Every increase of temperature arising from radiant heat is due to its absorption or reception into the body on which it falls. If a pencil of heat impinge on the surface of a body, through which no portion of it is directly transmitted, it must either be absorbed or reflected: those rays which are reflected cannot be absorbed; and those which are not reflected must be absorbed. The number of absorbed rays is supplemental to that of the reflected rays. It hence follows that as the reflecting power is materially influenced by the nature of surfaces, the absorptive power must be so likewise. Those qualities of a surface which increase reflection are to the same extent adverse to absorption; and those which favour absorption are proportionally injurious to reflection. Since, moreover, as was shown in the last article, the property of radiation is inversely as that of reflection, the power of radiating is directly proportional to that of absorbing heat. These inferences are fully justified by the researches of Leslie, and have received additional confirmation by a decisive experiment made by my colleague, Dr. Ritchie. (Royal Inst. Journal, v. 305.)

The colour of surfaces influences the absorption of radiant heat. This has been observed by several persons of the sun's rays, and of terrestrial heat associated with light, as will be stated in the next section; but the dependance of the absorptive power for simple heat on colour has not till lately been noticed. From researches by Stark already referred to (page 15), it seems that differently coloured wools wound upon the bulb of a thermometer, and exposed within a glass tube to hot water, rose from 50° to 170° in the following times,—black wool in 4′ 30″, dark green in 5′, scarlet in 5′ 30″, white in 8′.

An interesting connection has been traced by Nobili and Melloni between the absorbing and conducting power of surfaces. (An. de Ch. et Ph. xlviii. 198.) In their experiments variations of temperature were estimated by the *thermo-multiplier*, and these researches, if free from fallacy, justify the inference that the radiating and absorbing powers of surfaces for simple heat are in the inverse order of their conducting power.

Transmission of Heat.—Radiant heat passes with perfect freedom through a vacuum. The air and gaseous substances present but a feeble barrier to its progress; so feeble, indeed, that the degree of impediment which they occasion has not yet been appreciated. Most transparent media of a denser kind, on the contrary, such as the diamond, rock-crystal, glass, and water, even in thin strata, interfere greatly with its passage. This last remark, however, is only applicable to *simple radiant heat*, that is, to heat unassociated with light. The solar rays pass readily through glass, both heat and light being refracted in their passage, as is shown by the action of a burning glass or lens; and though much of the heat emitted by the flame of a lamp or a red-hot ball of iron is arrested by glass, many calorific rays are directly transmitted along with the light. But the result is different when the heated body is not luminous. A thin screen of glass interposed between such an object and a thermometer certainly intercepts most of the rays that fall upon it; and the sole question which can be raised is, whether the small effect on the thermometer is caused by direct transmission, or by the screen first becoming warm by absorbing the rays, and then acting by its radiation on the thermometer. On this point the philosophic world was long much divided; but the question has been at length finally set at rest by the masterly researches of Melloni, made with the thermo-multiplier (An. Ch. et Ph. xlviii. 198, liii. 5, lv. 337, lx. 402). He has proved that solids and liquids differ in transmissibility to the rays of heat, just as they differ in their action on light. This may be expressed by the terms *transcalent* and *intranscalent* (*trans* through, *caleo* I heat), or *diathermanous* and *adiathermanous* (*δια* through, *θεϱμαινω* I heat), corresponding to the adjectives transparent and opaque as applied to light. The principal conclusions flowing from his researches are the following:—

1. Though transcalent bodies are also in general more or less transparent, the only known exceptions being opaque black glass and black mica, yet the transcalency and transparency of a substance are not in the same proportion.

2. Radiant heat falling perpendicularly on laminæ of transcalent bodies having parallel surfaces suffers in all the same degree of reflection, which amounts to 39-1000ths of the incident rays on entering, and 37-1000ths on leaving the lamina.

3. Transcalent bodies differ in the degree of their transcalency. Rock-salt is the only known substance which is perfectly diathermanous: heat from any source falling on a lamina of pure rock-salt with parallel faces is not at all absorbed, all the rays which are not reflected being directly transmitted; and this is true whether the laminæ be thick or thin. The result is different with other transcalent bodies, which always absorb a portion of the incident rays. Of 100 rays of heat from the same source successively incident on laminæ of equal thickness of rock-salt, alum, flint-glass, and crown-glass, the transmitted rays were 92, 12, 65, and 49. Of 100 rays similarly incident on strata of water, chloride of sulphur, bisulphuret of carbon, ether, and alcohol, the transmitted rays were 11, 63, 63, 21, and 15. The rays transmitted through similar laminæ of coloured glass were 53 per cent. with violet glass, 47 with red, 34 with yellow, 33 with blue, and 26 with green glass.

4. In glass and liquids those are most transcalent which have the greatest refractive power in regard to light. This is shown in

No. 3, where only 11 per cent. of the incident heat passed through water, and 63 through a similar stratum of bisulphuret of carbon. But the law is not applicable to crystalline bodies: thus, as above, 92 per cent. of the incident rays find their way through rock-salt, and 12 per cent. through a similar stratum of alum; while their refractive powers for light are nearly the same.

5. The quantity of radiant heat transmissible through glass varies with the temperature of the source from which the rays emanate. Of 100 rays successively incident on the same lamina of glass from the four sources, an oil-lamp, red-hot platinum, blackened copper heated to 734°, and the same copper at 212°, the number of rays transmitted were 77, 57, 34, and 12. Similar results were formerly obtained by De la Roche (Biot's Traité de Physique, iv. 638); and Melloni has proved that diathermanous bodies in general act in the same manner as glass. The only exception is rock-salt, which is equally permeable to rays from sources of a low as of a high temperature. It further appears that rays from the same source pass through some media more readily than through others. It seems an unavoidable inference from Melloni's experiments, that radiant heat has different properties according to its source; that there are various kinds or states of radiant heat, just as there are various kinds or states of light as manifested by its different colours. The rays of light which have passed through blue glass will pass through a second blue glass more easily than through glass of a different colour, though otherwise less opaque than the blue glass. So do calorific rays, after transmission through water, pass through a second stratum of water more readily than through liquids otherwise more diathermanous, such as alcohol or ether. The water absorbs many rays which might have had the power to pass through alcohol, and gives passage to others which can penetrate water, but not alcohol. Hence it should follow, as Melloni has proved, that comparatively little heat is absorbed by multiplying screens of the same material, or increasing the thickness of one screen: it is the first screen, or the side of one screen, next the radiating substance, by which the principal absorption of heat is effected. The quantity of heat arrested by increasing the thickness of a screen decreases in a very rapid ratio. These facts establish between heat and light new and deeply interesting relations, which will be referred to in the next section.

6. Melloni has established the refrangibility of heat by diathermanous media. Prior observers failed of obtaining decisive evidence

of this property, in consequence of using prisms or lenses of glass the feeble transcalency of which unfits it for such an inquiry; but with a prism of rock-salt Melloni easily demonstrated the general principle, and proved that heat from different sources, like light of different colours, has different degrees of refrangibility.

Polarization and double Refraction of Heat.—These properties of radiant heat, which Melloni with all his skill vainly attempted to demonstrate, have lately been established in regard to heat, both from luminous and non-luminous sources, by Forbes,—a discovery of great interest, as drawing still closer the relations of heat and light, and for which he has received the well-merited honour of the Keith medal, awarded by the Royal Society of Edinburgh. Forbes has polarized heat by all the methods which polarize light, —by reflection, refraction, and double refraction. He also depolarized heat; and as this occurs only as a consequence of double refraction, he thereby proved the double refraction of heat. The instrument used by Forbes was the thermo-multiplier, brought to such extreme delicacy that it is supposed sensible to 1-1500ths of a degree of Fahrenheit's thermometer. (Phil. Trans. Ed. 1835.)

Theory of Radiation.—The tendency which all bodies evince to attain an equality of temperature by means of radiation, has given rise to two ingenious theories, suggested respectively by Pictet and Prevost. According to the former, bodies of equal temperature do not radiate at all; and when the temperature is unequal, the hotter give calorific rays to the colder bodies till an equilibrium is established, at which moment the radiation ceases. Prevost, on the contrary, conceived radiation to go on at all times, and from all substances, whether their temperature were the same or different from that of surrounding objects (Recherches sur la Chaleur). Consistently with this view, the temperature of a body falls whenever it radiates more heat than it absorbs; its temperature is stationary when the quantities emitted and received are equal; and it grows warm when the absorption exceeds the radiation. Of these theories the preference is very generally accorded to the latter.

Adopting, then, the theory of Prevost, it will be useful to examine a few instances of its application;—and, first, in regard to the experiments with conjugate mirrors. If a metallic ball in the focus of one mirror, and a thermometer in that of the other, be of the same temperature as the surrounding objects (say at 60°), the thermometer will remain stationary. It will indeed receive rays from the ball; but as it emits an equal number in return, its temperature will be unchanged. If the ball is above 60° the thermometer will rise, because it then receives a greater number of rays than it emits. If, on the contrary, the ball is below 60°, the thermometer, being the warmer of the two bodies, emits more rays than it receives, and its temperature will fall.

The same mode of reasoning explains an interesting experiment originally performed by the Florentine Academicians, and since carefully repeated by Pictet. He placed a piece of ice instead of the metallic ball in the focus of his mirror, and observed that the thermometer in the opposite focus immediately descended, but rose again as soon as the ice was removed. On replacing the ice in the focus, the thermometer again fell, and reascended when it was withdrawn. It was supposed by some philosophers that this experiment proved the existence of frigorific rays, endowed with the property of communicating coldness; whereas, all the preceding remarks were made on the supposition that cold is merely a negative quality arising from the diminution of heat. Nor is the foregoing experiment inconsistent with such an opinion: on the contrary, it is readily accounted for by the theory of Prevost, and might have been anticipated by its application. The thermometer, in fact, has its temperature lowered, because it emits more rays than it receives; and it rises when the ice is removed, because it then receives a number of calorific rays radiated by the warmer surrounding objects, which were intercepted by the ice while it was in the focus.

An elegant application of this theory was made by Dr. Wells to account for the formation of dew. The most copious deposit of dew takes place when the weather is clear and serene; and the substances that are covered with it are always colder than the contiguous strata of air, or than those bodies on which dew is not deposited. In fact, dew is a deposition of water previously existing in the air as vapour, and which loses its gaseous form only in consequence of being chilled by contact with colder bodies. In speculating, therefore, about the cause of this phenomenon, the chief object is to discover the cause of the reduction of temperature. The explanation proposed by Wells, in his excellent Treatise on Dew, and now universally adopted, is founded on the theory of Prevost. If it be admitted that bodies radiate at all times, their temperature can remain stationary only by their receiving from surrounding objects as many rays as they emit; and should a substance be so situated that its own radiation may continue uninterruptedly without an equivalent being returned to it, its temperature must necessarily fall. Such is believed to be the condition of the ground in a calm starlight evening. The calorific rays which are then emitted by substances on the surface of the earth, are dispersed through free space and lost: nothing is present in the atmosphere to exchange rays with them, and their temperature consequently diminishes. If, on the contrary, the weather be cloudy, the radiant heat proceeding from the earth is intercepted by the clouds, an interchange is established, and the ground retains nearly, if not quite, the same temperature as the adjacent portions of air.

All the facts hitherto observed concerning the formation of dew, tend to confirm this explanation. Dew is deposited sparingly or not at all in cloudy weather; all circumstances which promote free radiation are favourable to its deposition; good radiators of heat, such as grass, wood, the leaves of plants, and filamentous substances in general, reduce their temperature, in favourable states of the weather, to an extent of 10, 12, or even 15 degrees below that of the circumambient air; and while these are drenched with dew, pieces of polished metal, smooth stones, and other imperfect radiators, are barely moistened, and are nearly as warm as the air in their vicinity.

Cooling of Bodies. — Heated bodies cool by two very different methods (page 10). When a hot body is enveloped in solid substances, its heat is withdrawn solely by communication, and the velocity of cooling depends on the conducting power. Cooling is effected in a similar manner when the heated body is immersed in a liquid; but the velocity of cooling then depends partly on the conducting power of the liquid, and partly on the mobility of its particles. In elastic fluids the cooling takes place both by communication and radiation; and in a vacuum it is produced solely by radiation.

EFFECTS OF HEAT.

The phenomena that may be ascribed to this agent, and which may therefore be enumerated as its effects, are numerous. With respect to animals, it is the cause of the feelings of cold, agreeable warmth, and burning, according to its intensity. It excites the system powerfully, and without a certain degree of it the vital actions entirely cease. Over the vegetable world its influence is obvious to every eye. By its stimulus co-operating with air and moisture, the seed bursts its envelope and yields a new plant, the buds open, the leaves expand, and the fruit arrives at maturity. With the declining temperature of the seasons the circulation of the sap ceases, and the plant remains torpid till it is again excited by the stimulus of heat.

The dimensions of every kind of matter are regulated by this principle. Its increase, with few exceptions, separates the particles of bodies to a greater distance from each other, producing expansion, so that the same quantity of matter is thus made to occupy a larger space; and the diminution of heat has an opposite effect. Were the repulsion occasioned by this agent to cease entirely, the atoms of bodies would come into actual contact.

The form of bodies is dependent on heat. By its increase solids are converted into liquids, and liquids are dissipated in vapour; by its decrease vapours are condensed into liquids, and these become solid. If matter ceased to be under the influence of heat, all liquids, vapours, and doubtless even gases, would become permanently solid; and all motion on the surface of the earth would be arrested.

When heat is accumulated to a certain extent in bodies, they shine or became *incandescent*. On this important property depend all our methods of artificial illumination.

Heat exerts a powerful influence over chemical phenomena. There is, indeed, scarcely any chemical action which is not in some degree modified by this principle; and hence a knowledge of its laws is indispensable to the chemist. By its means bodies previously separate are made to combine, and the elements of compounds are disunited. An undue proportion of it is destructive to all organic and many mineral compounds; and it is essentially concerned in combustion, a process so necessary to the wants and comforts of man.

Of the various effects of heat above enumerated, several will be discussed in other parts of the work. In this place it is proposed to treat only of its influence over the dimensions and form of bodies, a subject which will be conveniently studied under the three heads of expansion, liquefaction, and vaporization.

EXPANSION.

One of the most remarkable properties of heat is the repulsion which exists among its particles, a property which enables it, on entering into a body, to remove the integrant molecules of the substance to a greater distance from each other. The body, therefore, becomes less compact than before, occupies a greater space, or in other words, expands. This effect of heat is opposed to cohesion—that force which tends to make the particles of matter approximate, and which must be overcome before any expansion can ensue. Heat, therefore, should produce the greatest expansion in those bodies which are least influenced by cohesion, an inference fully justified by observation. Thus the force of cohesion is greatest in solids, less in liquids, and least of all in aëriform substances; while the expansion of solids is trifling, that of liquids much more considerable, and that of elastic fluids far greater.

It may be laid down as a rule, the reason of which will now be obvious, that all bodies are expanded by heat, and that the expansion of the same body increases with the quantity of heat which enters it. But this law does not apply, unless the form and chemical constitution of the body is preserved. For if a change in either be occasioned, then the reverse of expansion may ensue; not, however, as the direct consequence of an augmented temperature, but as the result of a change in form or composition.

To prove the expansion of solids, we need only take the exact dimensions in length, breadth, and thickness, of any substance when cold, and measure it again while strongly heated, when it will be found to have increased in every direction. This dilatation from heat and consequent contraction in cooling take place with a force which appears to be irresistible.

The expansion of solids has engaged the attention of several experimenters, who have endeavoured to determine the exact quantity by which different substances are lengthened by a given increase of heat, and whether or not their elongation is equable at different temperatures. Their expansion, for example, from the freezing point of water to 122°, is equal to what takes place betwixt 122° and 212°. The researches of Dulong and Petit (An. de. C. et P. vii.) prove that solids do not dilate uniformly at high temperatures, but expand in an increasing ratio; that is, the higher the temperature beyond 212°, the greater the expansion for equal additions of heat. It is manifest, indeed, from their experiments, that the rate of expansion is an increasing one even between 32 and 212; but the differences which exist within this small range are so inconsiderable as to escape observation, and for most practical purposes may be disregarded.

The subjoined table includes the most interesting results of Lavoisier and Laplace, who have carefully investigated the linear expansion of solids. (Biot, i. 158.)

Names of Substances.	Elongation when heated from 32° to 212°.
Glass tube without lead, a mean of three specimens	$\frac{1}{1115}$ of its length.
English flint glass	$\frac{1}{1248}$
Copper	$\frac{1}{581}$
Brass—mean of two specimens	$\frac{1}{532}$
Soft iron forged	$\frac{1}{819}$
Iron wire	$\frac{1}{812}$
Untempered steel	$\frac{1}{927}$
Tempered steel	$\frac{1}{807}$
Lead	$\frac{1}{351}$
Tin of India	$\frac{1}{516}$
Tin of Falmouth	$\frac{1}{462}$
Silver	$\frac{1}{524}$
Gold—mean of three specimens	$\frac{1}{602}$
Platinum, determined by Borda	$\frac{1}{1167}$

Knowing the elongation of any substance for a given number of degrees of the thermometer, its total increase in bulk may in general be calculated by trebling the number which expresses its increase in length.

The expansion of liquids is proved by putting a common thermometer, made with mercury or alcohol, into warm water, when the dilatation of the liquid will be shown by its ascent in the stem. The experiment is indeed illustrative of two other facts. It proves, first, that the dilatation increases with the temperature; for if the thermometer be plunged into several portions of water heated to different degrees, the ascent will be greatest in the hottest water, and least in the coolest portions. It demonstrates, secondly, that liquids expand more than solids. The glass bulb of the thermometer is itself expanded by the hot water, and therefore is enabled to contain more mercury than before; but the mercury being dilated to a much greater extent, not only occupies the additional space in the bulb, but likewise rises in the stem. Its ascent marks the difference between its own dilatation and that of the glass, and is only the apparent, not the actual, expansion of the liquid.

Different liquids do not expand to the same degree from an equal increase of temperature. Alcohol expands much more than water, and water than mercury. From the frequency with which the latter is employed in philosophical experiments, it is important to know the exact amount of its expansion. This subject has been investigated by several philosophers, but the experiments of Lavoisier and Laplace, and especially of Dulong and Petit, from the extreme care with which they were made, are entitled to the greatest confidence. According to the former the actual dilatation of mercury, in passing from the freezing to the boiling point of water, amounts to $\frac{100}{5412}$ of its volume; but the result obtained by Dulong and Petit, who found it $\frac{100}{5550}$, is probably still nearer the truth. Adopting the last estimate, this metal dilates, for every degree of Fahrenheit's thermometer, $\frac{1}{9990}$ of the bulk which it occupied at the temperature of 32°. The apparent expansion of mercury contained in glass is of course less than the absolute expansion. Between the limits of 32° and 212° Lavoisier and Laplace estimate the apparent expansion at $\frac{1}{63}$, and Dulong and Petit at $\frac{1}{64\cdot8}$ of its volume, being $\frac{1}{11664}$ for each degree of Fahrenheit's thermometer.

All experimenters agree that liquids expand in an increasing ratio, or that equal increments of heat cause a greater dilatation at high than at low temperatures. Thus, if a fluid is heated from 32° to 122° it will not expand so much as it would do in being heated from 122° to 212°, though an equal number of degrees is added in both cases. In mercury the first expansion, according to Deluc, is to the second as 14 to 15; in olive oil as 13·4 to 15; in alcohol as 10·9 to 15; and in pure water as 4·7 to 15.

There is a peculiarity in the effect of heat upon the bulk of some fluids; namely, that at a certain temperature increase of heat causes them to contract, and its diminution makes them expand. This singular exception to the general effect of heat is only observable in those liquids which increase in bulk in passing from the liquid to the solid state, and is remarked only within a few degrees of temperature above their point of congelation. Water is a noted example of it. Ice swims upon the surface of water, and therefore must be lighter than it; a convincing proof that water in the act of freezing must expand. The specific gravity of ice is nearly 0·92, which gives the volume of ice to that of water as 1 to 0·92; that is, water expands by about 1-11th of its volume in passing into ice.

But it is not only during the act of congelation that water expands; since it begins to dilate some time before it actually freezes. Dr. Croune noticed this phenomenon so early as the year 1683, and it has since been observed by various philosophers. To render this obvious, fill a flask, capable of holding three or four ounces, with water at the temperature of 60°, and adapt to it a cork, through which passes a glass tube open at both ends, about the eighth of an inch wide, and ten inches long. After having filled the flask, insert the cork and tube, and pour a little water into the latter till the liquid rises to the middle of it. On immersing the flask into a mixture of pounded ice and salt, the water at first contracts, and therefore descends in the tube; but soon after an opposite movement ensues, indicating dilatation, though the water within the flask is at the same time yielding heat to the freezing mixture in which it is immersed.

To the inference deduced from this experiment it was objected, that the ascent of the water in the tube is not referable to expansion in the liquid, but to contraction of the flask, diminishing its capacity. In fact, this cause does operate, though not to a degree sufficient to account for the whole effect; and, accordingly, it has been proved by an elegant and decisive experiment of Dr. Hope, that water does really expand previous to congelation. He believes the greatest density of water to be between 39·5° 40°; that is, boiling water obeys the usual law till it has cooled to the temperature of about 40°, after which the abstraction of heat produces increase instead of decrease of volume (Phil. Trans. Ed. v. 379). Hallström, who has examined this point with much care, estimates it at 39°.

The cause of the expansion of water at the moment of freezing is attributed to a new and peculiar arrangement of its particles. Ice is in reality crystallized water, and during its formation the particles arrange themselves in ranks and lines, which cross each other at angles of 60° and 120°, and consequently occupy more space than when liquid. This may be seen by examining the surface of water while freezing in a saucer.

Water is not the only liquid which expands under reduction of temperature, as the same effect has been observed in a few others which assume a highly crystalline structure on becoming solid;—fused iron, antimony, zinc, and bismuth, are examples of it. Mercury is a remarkable instance of the reverse; for when it freezes, it suffers a very great contraction.

As the particles of air and aëriform substances are not held together by cohesion, it follows that increase of temperature must occasion a considerable dilatation of them; and, accordingly, they are found to dilate from equal additions of heat much more than solids or liquids.

This subject had been unsuccessfully investigated by several philosophers, who failed in their object chiefly because they neglected the precaution of drying the gases upon which they operated; but at last the law of dilatation was detected by Dalton and Gay-Lussac nearly at the same time.

It is proved by the researches of these philosophers, that all gases undergo equal expansions by the same addition of heat, supposing them placed under the same circumstances; so that it is sufficient to ascertain the law of expansion observed by any one gas, in order to know the law for all. The experiments of Gay-Lussac show that 100 parts of air in being heated from 32° to 212° expand to 137·5 parts. The increase for 180 degrees is therefore 0·375 or $\frac{37{\cdot}5}{100}$ths of its bulk; and by dividing this number by 180, it is found that a given quantity of dry air dilates to $\frac{1}{480}$th of the volume it occupied at 32°, for every degree of Fahrenheit's thermometer. The result of Dalton's experiments corresponds very nearly with the foregoing.

This point being established, it is easy to ascertain what volume any given quantity of gas should occupy at any given temperature. Suppose a certain portion of gas to occupy 20 measures of a graduated tube at 32°, it may be desirable to determine what would be its bulk at 42°. For every degree of heat it has increased by $\frac{1}{480}$th of its original volume, and therefore, since the increase amounts to ten degrees, the 20 measures will have dilated by $\frac{10}{480}$ths. The expression will therefore be $20 + 20 \times \frac{10}{480} = 20{\cdot}416$. The volume which the gas occupies at 32° is a necessary element in all such calculations. Thus, having 20·416 measures of gas at 42°, the corresponding bulk for 52° cannot be calculated by the formula $20{\cdot}416 + 20{\cdot}416\frac{10}{480}$; the real expression is $20{\cdot}416 + 20\frac{10}{480}$, because the increase is only $\frac{10}{480}$ths of the space occupied at 32°, which is 20 measures. A similar remark applies to the formula for estimating the effect of heat on the height of the barometer.

The rate of expansion of atmospheric air at temperatures exceeding 212° has been examined by Dulong and Petit, and the following table contains the result of their observations. (An. de Ch. et Ph. vii. 120.)

Temperature by the Mercurial Thermometer.		Corresponding volumes of a given volume of air.
Fahrenheit.	Centigrade.	
— 33	— 36..	0.8650
32	0..	1.0000
212	100..	1.3750
302	150..	1.5576
392	200..	1.7389
482	250..	1.9189
572	300..	2.0976
M. boils 680	360..	2.3125

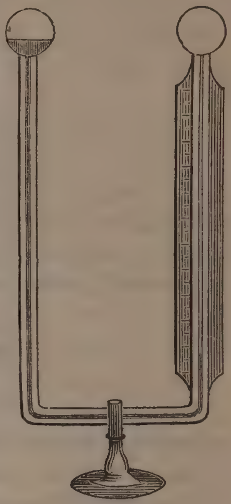
Hydrogen gas was found to expand in the same proportion, so that all gases may be inferred to expand to the same extent, for equal increments of heat, between —33° and 680°; and the same law probably prevails at all temperatures.

ON THE THERMOMETER.

The influence of heat over the bulk of bodies is better fitted for estimating a change in the quantity of that agent than any other of its properties; for substances not only expand more and more as the temperature increases, but in general return exactly to their original volume when the heat is withdrawn. The first attempt to measure the intensity of heat on this principle was made early in the seventeenth century, and the honour of the invention is by some bestowed on Sanctorius, by others on Cornelius Drebel, and by others on the celebrated Galileo. The material used by Sanctorius was atmospheric air. There are, however, two forcible objections to the general employment of this thermometer. In the first place, its dilatations and contractions are so great, that it is inconvenient to measure them when the change of temperature is considerable; and, secondly, its movements are influenced by pressure as well as by heat, so that the instrument would be affected by variations of the barometer, though the temperature should be quite stationary.

For the reasons just stated, the common air thermometer is rarely employed; but a modification of it, described in 1804 by Leslie in his Essay on Heat under the name of *Differential Thermometer*, is entirely free from the last objection, and is admirably fitted for some special purposes. This instrument was invented a century and a half ago by Sturmius, Professor of Mathematics at

Altdorff, who has left a description and sketch of it in his *Collegium Curiosum*, p. 54, published in the year 1676; but like other air thermometers it had fallen into disuse, till it was again brought into notice by Leslie. As now made it consists of two thin glass balls joined together by a tube, bent twice at a right angle, as represented in the annexed figure. Both balls contain air, but the greater part of the tube is filled with sulphuric acid coloured with carmine. It is obvious that this instrument cannot be affected by any change of temperature acting equally on both balls; for as long as the air within them expands or contracts to the same extent, the pressure on the opposite surfaces of the liquid, and consequently its position, will continue unchanged. Hence the differential thermometer stands at the same point, however different may be the temperature of the medium. But the slightest difference between the temperature of the two balls will instantly be detected; for the elasticity of the air on one side being then greater than that on the other, the liquid will retreat towards the ball whose temperature is lowest.



Solid substances are not better suited to the construction of a thermometer than gases; for while the expansion of the latter is too great, that of the former is so small that it cannot be measured except by the adaptation of complicated machinery. Liquids which expand more than the one and less than the other, are exempt from both extremes; and, consequently, we must search among them for a material with which to construct a thermometer. The principle of selection is plain. A material is required whose expansions are uniform, and whose boiling and freezing points are very remote from one another. Mercury fulfils these conditions better than any other liquid. No fluid can support a greater degree of heat without boiling than mercury; and none, except alcohol and ether, can endure a more intense cold without freezing. It has, besides, the additional advantage of being more sensible to the action of heat than other liquids, while its dilatations between 32° and 212° are almost perfectly uniform. Strictly speaking, the same quantity of heat does occasion a greater dilatation at high than at low temperatures, so that, like other fluids, it expands in an increasing ratio. But it is remarkable that this ratio, within the limits assigned, is exactly the same as that of glass; and therefore, if contained in a glass tube, the increasing expansion of the vessel compensates for that of the mercury.

We cannot here describe in detail the method of constructing a mercurial thermometer. This well known instrument consists of a tube of a uniform small bore, having a ball blown at one end. The ball and part of the tube are filled with mercury, the air is expelled by boiling the mercury, and the tube is hermetically sealed.

In order to graduate the thermometer, two fixed points are required: these are obtained by immersing it first in melting ice, marking the point at which it stands; and secondly in boiling water, at the level of the sea, and under the usual atmospheric pressure, the point at which it stands being also marked.

The distance between these two points may be divided into any number of equal parts or degrees. Fahrenheit, whose scale is commonly used in this country, divided it into 180 degrees, beginning his scale at a point 32 of these degrees below the freezing point of water, which is the zero of his scale. Celsius, the author of the centigrade scale, most frequently employed on the Continent, placed his zero at the freezing point, and divided the distance between that and the boiling point into 100 degrees. Reaumur adopted the same starting point or zero, but divided the same distance into 80 degrees only. Hence, the boiling point of water, on Fahrenheit's scale, is 212°, on the centigrade scale 100°, and on that of Reaumur 80°.

It is easy to reduce the temperature expressed by one thermometer to that of another, by knowing the relation which exists between their degrees. Thus, 180 is to 100 as 9 to 5, and to 80 as 9 to 4; so that nine degrees of Fahrenheit are equal to five of the centigrade, and four of Reaumur's thermometer. Fahrenheit's is therefore reduced to the centigrade scale, by multiplying by five, and dividing by nine; or to that of Reaumur, by multiplying by four instead of five, previously subtracting 32°, because the zero of Fahrenheit is 32° lower than that of the others. The same process, reversed, enables us to reduce degrees of the other scales to those of Fahrenheit.

But, to save the trouble of such reductions, I have subjoined a table which shows the degrees on the centigrade scale and that of Reaumur, corresponding to the degrees of Fahrenheit's thermometer.

Fahr.	Cent.	Reaum.	Fahr.	Cent.	Reaum.	Fahr.	Cent.	Reaum.
212	100	80	113	45	36	14	–10	– 8
203	95	76	104	40	32	5	–15	–12
194	90	72	95	35	28	4	–20	–16
185	85	68	86	30	24	–13	–25	–20
176	80	64	77	25	20	–22	–30	–24
167	75	60	68	20	16	–31	–35	–28
158	70	56	59	15	12	–40	–40	–32
149	65	52	50	10	8			
140	60	48	41	5	4			
131	55	44	32	0	0			
122	50	40	23	–5	–4			

The mercurial thermometer may be made to indicate temperatures which exceed 212°, or fall below zero, by continuing the degrees above and below those points. But as mercury freezes at 39 degrees below zero, it cannot indicate temperatures below that point; and indeed the only liquid which has been used for such purposes is alcohol. Our means of estimating high degrees of heat are as yet very unsatisfactory.

The instruments for measuring intense degrees of heat are called *pyrometers*, and must be formed either of solid or gaseous substances. The former alone have been hitherto employed, though the latter, from the greater uniformity with which they expand, are better calculated for the purpose. The action of most pyrometers depends on the elongation of a metallic bar by heat; and the difficulty in their construction consists in finding an infusible metal of uniform expansibility, and in measuring the degree of expansion with exactness. The best of these is Daniell's pyrometer, which, with a little practice, may be used with facility, and appears susceptible of very great precision. (Phil. Trans. 1830 and 31.) It consists of a bar of platinum or soft iron, so placed in a case of black lead earthenware, that when exposed to a high temperature, the bar, expanding more than the case, pushes forward an index of porcelain. The degree to which the index is pushed forward measures the expansion of the bar. Although the expansions of the bar be not strictly uniform at different temperatures, still they afford a good practical index of the relative intensity of different fires, and will be an exact measure of temperature when the precise rate of expansion shall have been determined.

The pyrometer of Wedgewood acts on a different principle, being founded on the property which clay, a compound of aluminous earth and water, possesses of gradually losing its water when exposed to an increasing temperature, and of contracting as the water is dissipated. This instrument, however, is no longer employed by scientific men, because its indications cannot be relied on. Every observation requires a separate piece of clay, and the observer is never sure that the contraction of the second piece, from the same heat, will be exactly similar to that of the first; especially as it is difficult to procure specimens of the earth, the composition of which is in every respect the same.

Though the thermometer is one of the most valuable instruments of philosophical research, it must be confessed that the sum of information which it conveys is very small. It does indeed point out a difference in the temperature of two or more substances with great nicety; but it does not indicate how much heat any body contains. The thermometer gives the same kind of information which may be discovered, though less accurately, by the feelings; it recognizes in bodies that state alone which affects the senses with an impression of heat or cold,—the condition expressed by the word *temperature.* All we learn by this instrument is, whether the temperature of one body is greater or less than that of another; and if there is a difference, it is expressed numerically, namely, by the degrees of the thermometer. But it must be remembered that these degrees are parts of an arbitrary scale, selected for convenience, without any reference whatever to the actual quantity of heat present in bodies.

A little reflection will evince the propriety of these remarks. If two glasses of unequal size be filled with water just taken from the same spring, the thermometer will stand in each at the same height, though their quantities of heat are certainly unequal. This observation naturally suggests the inquiry, whether different kinds of substances, whose temperatures as estimated by the thermometer are the same, contain equal quantities of heat,—if, for example, a pound of iron contains as much heat as a pound of water or mercury. The foregoing remark shows that equality in temperature is not necessarily connected with equality in quantity of heat; and the inference has been amply confirmed by experiment. If equal quantities of water are mixed together, one portion being at 100° and the other at 50°, the temperature of the mixture will be the arithmetical mean or 75°; that is, the 25 degrees lost by the warm water will exactly suffice to heat the cold water by the same number of degrees. It is hence inferred, that equal weights or measures of water of the same temperature contain equal quantities of heat; and the same is found to be true of other bodies. But if equal weights or equal bulks of *different* substances are employed, the result will be different. Thus, if a pint of mercury at 100° be mixed with a pint of water at 40°, the mixture will have a temperature of 60°, so that the 40 degrees lost by the former, heated the latter by 20 degrees only; and when, reversing the experiment, the water is at 100° and the mercury at 40°, the mixture will be at 80°, the 20 degrees lost by the former causing a rise of 40 in the latter. The fact is still more strikingly displayed by substituting equal weights for measures. For instance, on mixing a pound of mercury at 160° with a pound of water at 40°, a thermometer placed in the mixture will stand at 45°; but if the mercury be at 40° and the water at 160°, the mixture will have a temperature of 155°. If water at 100° be mixed with an equal weight of spermaceti oil at 40°, the mixture will be found at 80°; and when the oil is at 100° and the water at 40°, the temperature of the mixture will be only 60°.

It appears from these facts, that the same quantity of heat imparts twice as high a temperature to mercury as to an equal volume of water; that a similar proportion is observed with respect to equal weights of spermaceti oil and water; and that the heat which gives 5 degrees to water will raise an equal weight of mercury by 115 degrees, being the ratio of 1 to 23. Hence if equal quantities of heat be added to equal weights of water, spermaceti oil, and mercury, their temperatures in relation to each other will be expressed by the numbers 1, 2, and 23; or, what amounts to the same, in order to increase the temperature of equal weights of those substances to the same extent, the water will require 23 times more heat than the mercury, and twice as much as the oil. The peculiarity exemplified by these substances, and which it would be easy to illustrate by other examples, was first noticed by Black. It is a law admitted to be universal, and may be thus expressed: that *equal* quantities of different bodies require *unequal* quantities of heat to heat them equally. This difference in bodies was expressed by Black by the term *capacity* for heat, but the term *specific heat* is now generally preferred.

The singular fact of substances of equal temperature containing unequal quantities of heat naturally excites speculation about its cause, and various attempts have been made to account for it.

The explanation deduced from the views of Black is the following. He conceived that heat exists in bodies in two opposite states: in one it is supposed to be in chemical combination, exhibiting none of its ordinary characters, and remaining as it were concealed, without evincing any signs of its presence; in the other, it is free and uncombined, passing readily from one substance to another, affecting the senses in its passage, determining the height of the thermometer, and, in a word, giving rise to all the phenomena which are attributed to this active principle.

Though it would be easy to start objections to this ingenious conjecture, it has the merit of explaining phenomena more satisfactorily than any view that has been proposed in its place. It is entirely consistent with analogy. But in admitting the plausibility of this explanation, it is proper to remember that it is at present entirely hypothetical; and that the language suggested by an hypothesis should not be unnecessarily associated with the phenomena to which it owes its origin. Accordingly, the word *sensible* is better than *free* heat, and *insensible* preferable to *combined* or *latent* heat; for by such terms the fact is equally well expressed, and philosophical propriety strictly preserved.

It is of importance to know the specific heat of bodies. The most convenient method of discovering it, is by mixing different substances together in the way just described, and observing the relative quantities of heat requisite for heating them by the same number of degrees.

This method was first suggested by Black, and was afterwards practised to a great extent by Crawford and Irvine.* But the same knowledge may be obtained by reversing the process,—by noting the relative quantities of heat which bodies give out in cooling; for if water require 23 times more heat than mercury to raise its temperature by one or more degrees, it must also lose 23 times as much in cooling. The calorimeter of Lavoisier and Laplace is founded on this principle. In this instrument the heat given out by a hot body in cooling is measured by the quantity of ice liquefied by it. But although the principle is unexceptionable, there are difficulties in the application of it which render the calorimeter an incorrect instrument. It is, therefore, unnecessary here to describe it in detail.

The determination of the sp. heat of gaseous substances is a problem of importance, and has occupied the attention of several experimenters of great science and practical skill; but the inquiry is beset with so many difficulties that, in spite of the talent which has been devoted to it, our best results can be viewed as approximations only, requiring to be corrected by future research. Crawford first investigated this subject, but his results are admitted to have been erroneous, and need not here be cited. Lavoisier and Laplace, by means of the calorimeter, obtained more accurate results; but those most to be depended on were obtained by Delaroche and Bérard by means of a modification of the calorimeter, in which they observed, not how much ice was melted, but how far water was heated by the hot body during its cooling. Their experiments were made with such skill as to inspire great confidence. They are contained in the following table; the sp. heat of the gases being referred to air as unity in the two first columns, and to water in the third.

---

* Crawford on Animal Heat, and Irvine's Chemical Essays.

Names of Substances.	Under equal Volumes and constant Pressure.	Under equal Weights.	
Atmospheric air	1·0000	1·0000	0·2669
Hydrogen gas	0·9033	12·3400	3·2936
Oxygen gas	0·9765	0·8848	0·2361
Nitrogen gas	1·0000	1·0318	0·2754
Nitrous oxide gas	1·3503	0·8878	0·2369
Olefiant gas	1·5530	1·5763	0·4207
Carbonic oxide gas	1·0340	1·0805	0·2884
Carbonic acid gas	1·2583	0·8280	0·2210
Water			1·0000
Aqueous vapour			0·8470

Although objections have been started to these experiments, and other methods of ascertaining the sp. heats of gases proposed by Haycraft, Delarive and Marcet, and others; yet on the whole we may conclude that, although the sp. heats of the gases are not accurately known, the numbers of Delaroche and Bérard are probably the best approximations hitherto published.

The circumstances which merit particular notice, concerning the sp. heats of bodies, may be arranged under the eight following heads:—

1. Every substance has a sp. heat peculiar to itself; whence it follows, that a change of composition will be attended by a change of sp. heat.

2. The sp. heat of a body varies with its form. A solid has a smaller sp. heat than the same substance when in the state of a liquid; the sp. heat of water, for instance, being 9 in the solid state, and 10 in the liquid. Whether the same weight of a body has a greater sp. heat in the solid or liquid form than in that of vapour, is a circumstance not yet decided.

3. When a given weight of any gas is made to vary in density and volume while its elasticity is unchanged, as when air confined in a tube over mercury is heated and suffered to expand without variation of pressure, the sp. heat is believed to remain constant.

4. Of the sp. heats of equal volumes of the same gas at a varying density and elasticity, as when air is forced into a bottle with different degrees of force, nothing certain has been established.

5. The sp. heats of equal weights of the same gas vary as the density and elasticity vary. Thus, when 100 measures of air expand by diminished pressure to 200 measures, its sp. heat is increased; and when the same quantity of air is compressed into the space of 50 measures, its sp. heat is diminished. The exact rate of increase is unknown; but, according to Delaroche and Bérard, the ratio is less rapid than the diminution in density; that is, the sp. heat of any gas being 1, it is not 2, but between one and two, when its volume is doubled.

6. The sp. heats of solids and liquids were formerly thought, especially by Crawford and Irvine, to be constant at all temperatures, so long as they suffer no change of form or composition Dalton, however, (Chemical Philosophy, part I. p. 50,) endeavours to show that the sp. heats of such bodies are greater in high than at low temperatures; and Petit and Dulong, in the essay already quoted, have proved it experimentally with respect to several of them.

It is difficult to determine whether the increased sp. heat observed in solids and liquids at high temperatures is owing to the accumulation of heat within them, or to their dilatation. It is ascribed in general to the latter, and I believe correctly; because the expansion and contraction of gases by change of pressure, without the aid of heat, is attended with corresponding changes of sp. heat.

7. Change of sp. heat always occasions a change of temperature. Increase in the former is attended by diminution of the latter; and decrease in the former, by increase of the latter. The explanation of these facts is obvious. In the first case, a quantity of heat

becomes insensible, which was previously in a sensible state; in the second, heat is evolved, which was previously latent.

8. An important relation between the sp. heats of some elementary substances and their equivalents was discovered by Dulong and Petit, namely, that the product of the sp. heat of each element by the weight of its atom is a constant quantity. This relation, if general, would be of great interest, as leading directly to the inference that the atoms of elementary substances are associated with equal quantities of heat, and enabling chemists to calculate either the sp. heats of elements from their equivalents, or conversely their equivalents from their sp. heats. (An. de Ch. et Ph. x. 403.) The relation above alluded to was exemplified by Dulong and Petit by a table similar to the subjoined.

	Specific Heat.		Relative Weights of Atoms.		Product of the Sp. Heat of each element by the weight of its atom.
Lead	0·0293	×	103·6	=	3·0353
Tin	0·0514	×	57·9	=	2·9760
Zinc	0·0927	×	32·3	=	2·9942
Tellurium	0·0912	×	32·3	=	2·9457
Copper	0·0949	×	31·6	=	2·9988
Nickel	0·1035	×	29·5	=	3·0532
Iron	0·1100	×	28	=	3·0800
Sulphur	0·1880	×	16·1	=	3·0268
Platinum	0·0355	×	98·8	=	3·3098
Bismuth	0·0288	×	71	=	2·0448
Cobalt	0·1498	×	29·5	=	4·4191
Arsenic	0·081	×	37·7	=	3·0537
Carbon	0·25	×	6·12	=	1·5300
Iodine	0·089	×	126·3	=	11·2407
Phosphorus	0·385	×	15·7	=	6·0445
Mercury	0·0330	×	202	=	6·6660
Silver	0·0557	×	108	=	6·0156
Gold	0·0298	×	199·2	=	5·9361

It will be observed, on inspecting the last column of the table, that the product of the sp. heat into the equivalent is very nearly 3 for the first nine substances. Platinum deviates visibly from the law; and bismuth, cobalt, and iodine, strikingly. The four last elements would nearly coincide with the law, were their respective equivalents estimated at half the numbers given in the tables, as would carbon were its equivalent doubled. These coincidences are too close and numerous to arise from chance, and justify a belief in the law having a real foundation dependent on the connection between heat and the elementary particles of matter. The researches of Avogadro and Neumann give additional weight to this opinion by tracing the same law in many compound bodies, those compounds alone being compared together whose atomic constitution is similar (An. de Ch. et Ph. LV. 80, and LVII. 113; and Pog. An. XXIII. 1).

ON LIQUEFACTION.

All bodies are solid, liquid, or gaseous; and the form they assume depends on the relative intensity of cohesion and repulsion. Should the repulsive force be comparatively feeble, the particles will adhere so firmly together, that they cannot move freely upon one another, thus constituting a solid. If cohesion is so far counteracted by repulsion, that the particles move on each other freely, a liquid is formed. And should the cohesive attraction be entirely overcome, so that the particles not only move freely on each other, but would, unless restrained by external pressure, separate from one another to an almost indefinite extent, an aëriform substance will be produced.

Now the property of repulsion is manifestly owing to heat; and as it is easy within certain limits to increase or diminish the quantity of this principle in any substance, it follows that the form of bodies may be made to vary at pleasure: that is, by heat sufficiently intense every solid may be converted into a fluid, and every fluid into vapour. This inference is so far justified by experience, that it may safely be considered as a law. The converse ought also to be true; and, accordingly, several of the gases have already been condensed into liquids by means of pressure, and liquids have been solidified by cold. The temperature at which liquefaction takes place is called the melting point, or point of fusion; and that at which liquids solidify, their point of congelation. Both these points are different for different substances, but uniformly the same, under similar circumstances, in the same body.

The most important circumstance relative to liquefaction is Black's discovery that a large quantity of heat disappears, or becomes insensible to the thermometer, during the process. If a pound of water at 32° be mixed with a pound of water at 172°, the temperature of the mixture will be intermediate between them, or 102°. But if a pound of water at 172° be added to a pound of ice at 32°, the ice will quickly dissolve, and on placing a thermometer in the mixture, it will be found to stand, not at 102°, but at 32°. In this experiment, the pound of hot water, which was originally at 172°, actually loses 140 degrees of heat, all of which enters into the ice, and causes its liquefaction, but without affecting its temperature; whence it follows that a quantity of heat becomes insensible during the melting of ice, sufficient to raise the temperature of an equal weight of water by 140 degrees. This explains the well-known fact, on which the graduation of the thermometer depends, — that the temperature of melting ice or snow never exceeds 32°. All the heat which is added becomes insensible, till the liquefaction is complete.

The loss of sensible heat which attends liquefaction seems essentially necessary to the change, and for that reason is frequently called the *heat of fluidity.* The actual quantity of heat required for this purpose varies with the substance, as is proved by the following results obtained by Irvine. The degrees indicate the extent to which an equal weight of each material may be heated by the heat of fluidity which is proper to it.

	Heat of Fluidity.
Sulphur	143°68F.
Spermaceti	145°
Lead	162°
Bees-wax	175°
Zinc	493°
Tin	500°
Bismuth	550°

As so much heat disappears during liquefaction, it follows that heat must be evolved when a liquid passes into a solid. This may easily be proved. The temperature of water in the act of freezing remains at 32°, though exposed to an atmosphere in which the thermometer is at zero. That the water under such circumstances may preserve its temperature, heat must be supplied as fast as it is abstracted; and it is obvious that the only source of supply is the heat of fluidity. Further, if pure recently boiled water be cooled very slowly, and kept very tranquil, its temperature may be lowered to 21° without any ice being formed; but the least motion causes it to congeal suddenly, and in doing so its temperature rises to 32°. (Blagden in Phil. Trans. 1788.)

The explanation which Black gave of these phenomena constitutes what is called his *doctrine* of *latent heat*, which was partially explained on a former occasion (page 35). He conceived that heat in causing fluidity loses its property of acting on the thermometer in consequence of combining chemically with the solid substance, and that liquefaction results, because the compound so formed does not possess that degree of cohesive attraction on which solidity depends. When a liquid is cooled to a certain point, it parts with its heat of fluidity, which is set free or becomes sensible, and the cohesion natural to the solid is restored. The same mode of reasoning was applied by Black to the conversion of liquids into vapours, a change during which a large quantity of heat disappears.

A different explanation of the phenomena was proposed by Irvine. Observing that a solid has a smaller sp. heat than the same substance while liquid, he argued that this circumstance alone accounts for heat becoming insensible during liquefaction. For since the sp. heat of ice and water, or in other words, the quantity of heat required to raise their temperature by the same number of degrees, was found to be as 9 to 10, Irvine inferred that ice must contain one-tenth less heat than water of the same temperature, and that as this difference must be supplied to the ice when it is converted into water, the change must necessarily be accompanied with the disappearance of heat. Irvine applied the same argument to the liquefaction of all solids, and likewise to account for the heat which is rendered insensible during the formation of vapour.

Two objections may properly be urged against the opinion of Irvine. In the first place, no adequate reason is assigned for the liquefaction. It accounts for the disappearance of heat which accompanies liquefaction, but does not explain why the body becomes liquid; whereas the hypothesis of Black affords an explanation both of the change itself, and of the phenomena that attend it. But the second objection is still more conclusive. Irvine argued on the belief that a liquid has in every case a greater sp. heat than when solid; and though this point has not been demonstrated in a manner entirely decisive, yet from the experiments hitherto made, it appears that liquids in general have greater sp. heats than solids, and that therefore Irvine's assumption is probably correct in regard to them. In like manner he believed vapours to have greater sp. heats than the liquids that yield them; but from the fact of most gases having smaller sp. heats than liquids, it is probable that the sp. heats of elastic fluids in general are inferior to those of the liquids from which they are derived. The disappearance of heat during vaporization is not explicable on the views of Irvine; it is necessary to employ the theory of Black to account for that change, and therefore the same doctrine should be applied to the analogous phenomenon of liquefaction.

The loss of sensible heat in liquefaction is the basis of many artificial processes for producing cold, all of which are founded on the principle of liquefying solid substances without supplying heat. The heat of fluidity being then derived from that which had previously existed within the solid itself in a sensible state, the temperature necessarily falls. The degree of cold thus produced depends upon the quantity of heat which disappears; and this again is dependent on the quantity of solid matter liquefied, and on the rapidity of liquefaction.

The most common method of producing cold is by mixing together equal parts of snow and salt. The salt causes the snow to melt by reason of its affinity for water, and the water dissolves the salt; so that both of them become liquid. The cold thus generated is 32 degrees below the temperature of freezing water; that is, a thermometer placed in the mixture would stand at zero. This is the way originally proposed by Fahrenheit for determining the commencement of his scale.

Any other substances which have a strong affinity for water may be substituted for the salt; and those have the greatest effect in producing cold whose affinity for that liquid is greatest, and which consequently produce the most rapid liquefaction. Crystallized chloride of calcium, proposed by Löwitz, is by far the most convenient in practice. It may be made by dissolving marble in hydrochloric acid, and concentrating the solution by evaporation, till, upon letting a drop of it fall upon a cold saucer, it becomes a solid mass. It should then be withdrawn from the fire, and when cold be speedily reduced to a fine powder. From its extreme deliquescence it must be preserved in well-stopped vessels. The following table by Mr. Walker contains the best proportions for producing intense cold. (Phil. Trans. 1801.)

FRIGORIFIC MIXTURES WITH SNOW.*

MIXTURES.	Parts by Weight.	Thermometer sinks.		Degree of Cold produced.
Sea-salt Snow	1 2	From any Temperature	to —5°	
Sea-salt Hydrochlorate of Ammonia Snow	2 1 5		to —12°	
Sea-salt Hydrochlorate of Ammonia Nitrate of Potassa Snow	10 5 5 24		to —18°	
Sea-salt Nitrate of Ammonia Snow	5 5 12		to —25°	

---

* The snow should be freshly fallen, dry, and uncompressed. If snow cannot be had, finely pounded ice may be substituted for it.

MIXTURES.	Parts by Weight.	Thermometer sinks.	Degree of Cold produced.
Diluted Sulphuric Acid * Snow	2 3	from +32° to —23°	55 degrees.
Concentrated Hydrochloric Acid Snow	5 8	from +32° to—27°	59
Concentrated Nitrous Acid Snow	4 7	from +32° to—30°	62
Chloride of Calcium Snow	5 4	from +32° to—40°	72
Crystallized Chloride of Calcium Snow	3 2	from +32° to—50°	82
Fused Potassa Snow	4 3	from +32° to—51°	83

Freezing mixtures are also made by the rapid solution of salts, without the use of snow or ice; the following table, by Walker, includes the most important of them. The salts must be finely powdered and dry. (Phil. Trans. 1795.)

MIXTURES.	Parts by Weight.	Temperature falls.	Degree of Cold produced.
Hydrochlorate of Ammonia Nitrate of Potassa Water	5 5 16	from +50° to +10°	40 degrees.
Hydrochlorate of Ammonia Nitrate of Potassa Sulphate of Soda Water	5 5 8 16	from +50° to +4°	46
Nitrate of Ammonia Water	1 1	from +50° to +4°	46
Nitrate of Ammonia Carbonate of Soda Water	1 1 1	from +50° to —7°	57
Sulphate of Soda Diluted Nitrous Acid †	3 2	from +50° to —3°	53
Sulphate of Soda Hydrochlorate of Ammonia Nitrate of Potassa Diluted Nitrous Acid	6 4 2 4	from +50° to—10°	60
Sulphate of Soda Nitrate of Ammonia Diluted Nitrous Acid	6 5 4	from +50° to—14°	64
Phosphate of Soda Diluted Nitrous Acid	9 4	from +50° to—12°	62
Phosphate of Soda Nitrate of Ammonia Diluted Nitrous Acid	9 6 4	from +50° to—21°	71
Sulphate of Soda Hydrochloric Acid	8 5	from +50° to 0°	50
Sulphate of Soda Diluted Sulphuric Acid ‡	5 4	from +50° to +3°	47

---

* Made of strong acid, diluted with half its weight of snow or distilled water.

† Composed of fuming nitrous acid 2 parts in weight, and one of water; the mixture being allowed to cool before being used.

‡ Composed of equal weights of strong acid and water, being allowed to cool before use.

These artificial processes for generating cold are much more effectual when the materials are previously cooled by immersion in other frigorific mixtures. One would at first suppose that an unlimited degree of cold might be thus produced; but it is found that when the difference between the mixture and the air becomes very great, the communication of heat from one to the other becomes so rapid, as to put a limit to the reduction. The greatest cold produced by Walker did not exceed 100 degrees below the zero of Fahrenheit.

Though we shall probably never succeed in depriving any substance of all its heat, bodies doubtless contain a certain definite quantity of this principle, and various attempts have been made to calculate its amount.

To be satisfied that such calculations cannot be trusted, it is sufficient to know that the estimates made by different chemists respecting the absolute quantity of heat in water vary from 900 to nearly 8000.*

VAPORIZATION.

Aëriform substances are commonly divided into vapours and gases. The former are characterised by their ready conversion into liquids or solids, either by a moderate increase of pressure, the temperature at which they were formed remaining the same, or by a moderate diminution of that temperature, without change of pressure. Gases, on the contrary, retain their elastic state more obstinately: they are always gaseous at common temperatures; and, with one or two exceptions, cannot be made to change their form, unless by being subjected to much greater pressure than they are naturally exposed to. Several of them, indeed, have hitherto resisted every effort to compress them into liquids. The only difference between gases and vapours is in the relative forces with which they resist condensation.

Heat is the cause of vaporization as well as of liquefaction. A sufficiently intense heat would doubtless convert every liquid and solid into vapour. Some bodies, however, resist the strongest heat of our furnaces without vaporizing. These are said to be *fixed* in the fire; those which, under the same circumstances, are converted into vapour, are called *volatile*.

The disposition of various substances to yield vapour is very different; and the difference depends doubtless on the relative power of cohesion with which they are endowed. Fluids, in general, are more easily vaporized than solids, as would be expected from the weaker cohesion of the former. Some solids, such as arsenic and sal-ammoniac, pass at once into vapour without being liquefied; but most of them become liquid before assuming the elastic condition.

---

* Dalton's New System of Chemical Philosophy.

Vapours occupy more space than the substances from which they were produced. Gay-Lussac found that water, in passing from its point of greatest density into vapour, expands to 1696 times its volume, alcohol to 659 times, and ether to 443 times, each vapour being at 212° and under a pressure of 29·92 inches of mercury. This shows that vapours differ in density. Watery vapour is lighter than air at the same temperature and pressure in the ratio of 1000 to 1604; or the sp. gr. of air being 1000, that of watery vapour is 625. The vapour of alcohol, on the contrary, is half as heavy again as air; and that of ether is more than twice and a half as heavy.

The dilatation of vapours by heat was found by Gay-Lussac to follow the same law as gases; that is, for every degree of Fahrenheit, they increase by $\frac{1}{480}$th of the volume they occupied at 32°. But this law only holds of vapours when separated from the liquids that yield them. If liquid be present heat not only expands the vapour but increases its volume by the addition of a new quantity of vapour. In like manner, the contraction of a vapour by cold will deviate from the above law, as soon as the cold condenses any part of it into liquid.

Vapours vary in volume under varying pressure according to the same law as gases, provided always that the gaseous state is preserved. This law, which was discovered by Boyle and Mariotte, and is more fully explained in the section on atmospheric air, merely expresses the fact that the volume of gaseous substances at a constant temperature is inversely as the pressure to which they are subject.

Vaporization is conveniently studied under two heads,—*Ebullition* and *Evaporation*. In the first, the production of vapour is so rapid that its escape gives rise to a visible commotion in the liquid; in the second, it passes off quietly and insensibly.

EBULLITION.

The temperature at which vapour rises with sufficient freedom for causing the phenomena of ebullition, is called the *boiling point.* The heat requisite for this effect varies with the nature of the fluid. Thus, sulphuric ether boils at 96°, alcohol at 176°, and pure water at 212°; while oil of turpentine must be raised to 316°, and mercury to 662°, before either exhibits marks of ebullition. The boiling point of the same liquid is constant, so long as the necessary conditions are preserved; but it is liable to be affected by several circumstances. The nature of the vessel has some influence upon it. Thus Gay-Lussac observed that pure water boils precisely at 212° in a metallic vessel, and at 214° in one of glass, owing apparently to its adhering to glass more powerfully than to a metal. It is likewise affected by the presence of foreign particles: when a few iron filings are thrown into water boiling in a glass vessel, its temperature quickly falls from 214° to 212°, and remains stationary at the latter point. But the circumstance which has the greatest influence over the boiling point of liquids is variation of pressure. All bodies upon the earth are constantly exposed to considerable pressure; for the atmosphere itself presses with a force equivalent to a weight of 15 pounds on every square inch of surface. Liquids are exposed to this pressure as well as solids, and their tendency to take the form of vapour is very much counteracted by it. In fact, they cannot enter into ebullition at all, till their particles have acquired such elastic force as enables them to overcome the pressure upon their surfaces; that is, till they press against the atmosphere with the same force as the atmosphere against them. Now the atmospheric pressure is variable, and hence it follows that the boiling point of liquids must also vary.

The pressure of the atmosphere is equal to a weight of 15 pounds on every square inch of surface, when the barometer stands at 30 inches, and then only does water boil at 212°. If the pressure be less, that is, if the barometer fall below 30 inches, then the boiling point of water and every other liquid will be lower than usual; or if the barometer rise above 30 inches, the temperature of ebullition will be proportionally increased. On this account water boils at a lower temperature on the top of a hill than in the valley beneath it; for as the column of air diminishes in length as we ascend, its pressure must likewise suffer a proportional diminution. The ratio between the depression of the boiling point and the diminution of the atmospheric pressure is so exact, that it has been proposed as a method for determining the heights of mountains. An elevation of 530 feet makes a diminution of one degree. (Wollaston in Phil. Trans. for 1817.)

The influence of the atmosphere over the point of ebullition is best shown by removing its pressure altogether. Robison found that fluids boil *in vacuo* at a temperature 140° lower than in the open air. (Black's Lectures, I. 151.)

Water cannot be heated under common circumstances beyond 212°, because it then acquires such expansive force as enables it to overcome the atmospheric pressure, and fly off in the form of vapour. But if subjected to sufficient pressure, it may be heated to any extent without boiling. This is best done by heating water while confined in a strong copper vessel, called Papin's Digester. In this apparatus, on the application of heat, a large quantity of vapour collects above the water, and checks ebullition by the pressure which it exerts upon the surface of the liquid. There is no limit to the degree to which water may thus be heated, provided the vessel is strong enough to confine the vapour; but the expansive force of steam under these circumstances is so enormous as to overcome the greatest resistance.

Robison (Brewster's edition of his works, p. 25) found that the tension of steam is equal to two atmospheres at 244°, and to three at 270°. The results of Southern's experiments, given in the same volume, fix upon 250·3° as the temperature of which steam has the force of two atmospheres, on 293·4° for four, and 343·6° for eight atmospheres.

This subject has been examined by a commission appointed by the Parisian Academy of Sciences, and Dulong and Arago took a leading part in the inquiry. The results, which are given in the following table, were obtained by experiment up to a pressure of 25 atmospheres, and at higher pressures by calculation. (Brande's Journal, N. S. viii. 191.)

Elasticity of the vapour, taking atmospheric press. as unity.	Temperature according to Fahrenheit.
1	212
1½	233·96
2	250·52
2½	263·84
3	275·18
3½	285·08
4	293·72
4½	300·28
5	307·5
5½	314·24
6	320·36
6½	326·26
7	331·70
7½	336·86

Elasticity of the vapour, taking atmospheric press. as unity.	Temperature according to Fahrenheit.	Elasticity of the vapour, taking atmospheric press. as unity.	Temperature according to Fahrenheit.
8	341·78	20	418·46
9	350·78	21	422·96
10	358·88	22	427·28
11	366·85	23	431·42
12	374·00	24	435·56
13	380·66	25	439·34
14	386·94	30	457·16
15	392·86	35	472·73
16	398·48	40	486·59
17	403·82	45	491·14
18	408·92	50	510·60
19	413·78		

The elasticity of steam is employed as a moving power in the steam-engine. The construction of this machine depends on two properties of steam, namely, the expansive force communicated to it by heat, and its ready conversion into water by cold.

The formation of vapour is attended, like liquefaction, with loss of sensible heat. This is proved by the well-known fact that the temperature of steam is precisely the same as that of the boiling water from which it rises; so that all the heat which enters into the liquid is solely employed in converting a portion of it into vapour, without affecting the temperature of either, provided the latter is permitted to escape with freedom. The heat, which then becomes latent, to use the language of Black, is again set free when the vapour is condensed into water. The exact quantity of heat rendered insensible by vaporization may therefore be ascertained by condensing the vapour in cold water, and observing the rise of temperature which ensues. From the experiments of Black and Watt, conducted on this principle, steam of 212°, in being condensed into water of 212°, gives out as much heat as would raise the temperature of an equal weight of water by 950 degrees, all of which had previously existed in the vapour without being sensible to a thermometer.

The latent heat of steam and several other vapours has been examined by Dr. Ure, whose results are contained in the following table. (Phil. Trans. for 1818.)

	Latent heat.
Vapour of water at its boiling point .	967°
Alcohol . . .	442
Ether . . .	302·379
Petroleum . . .	177·87
Oil of Turpentine .	177·87
Nitric acid . . .	531·99
Liquid ammonia . .	837·28
Vinegar . . .	875

The disappearance of heat that accompanies vaporization was explained by Black and Irvine, in the way already mentioned under the head of liquefaction; and as the objections to the views of Irvine were then stated, it is unnecessary to mention them on the present occasion.

The variation of volume and elasticity in vapours is attended, as in gases, with a change of sp. heat and a consequent variation of temperature (page 37). Thus when steam, highly heated and compressed in a strong boiler, is permitted to escape by a large aperture, the sudden expansion is attended with a great loss of sensible heat: its temperature instantly sinks so much, that the hand may be held in the current of vapour without inconvenience. The same principle accounts for the fact, first ascertained by Watt, that distillation at a low temperature is not attended with any saving of fuel. For when water boils at a low temperature in a vacuum, the vapour is in a highly expanded state, and contains more insensible heat than steam of greater density.

EVAPORATION.

Evaporation as well as ebullition consists in the formation of vapour, and the only assignable difference between them is, that the one takes place quietly, the other with the appearance of boiling. Evaporation occurs at common temperatures. This fact may be proved by exposing water in a shallow vessel to the air for a few days, when it will gradually diminish, and at last disappear entirely. Most fluids, if not all of them, are susceptible of this gradual dissipation; and it may also be observed in some solids, as for example in camphor. Evaporation is much more rapid in some fluids than in others, and it is always found that those liquids the boiling point of which is lowest evaporate with the greatest rapidity. Thus alcohol, which boils at a lower temperature than water, evaporates also more freely; and ether, whose point of ebullition is yet lower than that of alcohol, evaporates with still greater rapidity.

The chief circumstances that influence the process of evaporation are extent of surface, and the state of the air as to temperature, dryness, stillness, and density.

1. Extent of surface. Evaporation proceeds only from the surface of fluids, and therefore, *cæteris paribus*, must depend upon the extent of surface exposed.

2. Temperature. The effect of heat in promoting evaporation

may easily be shown by putting an equal quantity of water into two saucers, one of which is placed in a warm, the other in a cold situation. The former will be quite dry before the latter has suffered appreciable diminution.

3. State of the air as to dryness or moisture. When water is covered by a stratum of dry air, the evaporation is rapid even when its temperature is low. Thus in dry cold days in winter, the evaporation is exceedingly rapid; whereas it goes on very tardily, if the atmosphere contain much vapour, even though the air be very warm.

4. Evaporation is far slower in still air than in a current, and for an obvious reason. The air immediately in contact with the water soon becomes moist, and thus a check is put to evaporation. But if the air be removed from the surface of the water as soon as it has become charged with vapour, and its place supplied with fresh dry air, then the evaporation continues without interruption.

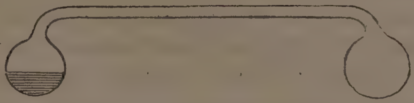
5. Pressure on the surface of liquids has a remarkable influence over evaporation. This is easily proved by placing ether in the vacuum of an air-pump, when vapour rises so abundantly as to produce ebullition.

As a large quantity of heat passes from a sensible to an insensible state during the formation of vapour, it follows that cold should be generated by evaporation. The fact may readily be proved by letting a few drops of ether evaporate from the hand, when a strong sensation of cold will be excited; or if the bulb of a thermometer, covered with lint, be moistened with ether, the production of cold will be marked by the descent of the mercury. But to appreciate the degree of cold which may be produced by evaporation, it is necessary to render it very rapid and abundant by artificial processes; and the best means of doing so is by removing pressure from the surface of volatile liquids. Water placed under the exhausted receiver of an air-pump evaporates with great rapidity, and so much cold is generated as would freeze the water, did the vapour continue to rise for some time with the same velocity. But the vapour itself soon fills the vacuum, and retards the evaporation by pressing upon the surface of the water. This difficulty may be avoided by putting under the receiver a substance, such as sulphuric acid, which has the property of absorbing watery vapour, and consequently of removing it as quickly as it is formed. Such is the principle of Leslie's method for freezing water by its own evaporation.*

---

* See art. Cold, in the Supplement to the Encyclopædia Britannica.

The action of the cryophorus, an ingenious contrivance of the late Dr. Wollaston, depends on the same principle. It consists of two glass balls, perfectly free from air, and joined together by a tube as here represented.—One of the balls contains a portion of distilled water, while the other parts of the instrument, which appear empty, are full of aqueous vapour, which checks the evaporation from the water by the pressure it exerts upon its surface. But when the empty ball is plunged into a freezing mixture, all the vapour within it is condensed; evaporation commences from the surface of the water in the other ball, and it is frozen in two or three minutes by the cold thus produced.



Liquids which evaporate more rapidly than water, cause a still greater reduction of temperature. The cold produced by the evaporation of ether in the vacuum of the air-pump is so intense as, under favourable circumstances, to freeze mercury.*

Scientific men have differed concerning the cause of evaporation. It was once supposed to be owing to chemical attraction between the air and water, and the idea is at first view plausible, since a certain degree of affinity does to all appearance exist between them. But it is nevertheless impossible to attribute the effect to this cause. For evaporation takes place equally *in vacuo* as in the air; nay, it is an established fact, that the atmosphere positively retards the process, and that one of the best means of accelerating it is by removing the air altogether. The experiments of Dalton prove that heat is the true and only cause of the formation of vapour. He finds that the actual quantity of vapour which can exist in any given space is dependent solely upon the temperature.

Dalton also found that the tension or elasticity of vapour is always the same, however much the pressure may vary, so long as the temperature remains constant, and there is liquid enough present to preserve the state of saturation proper to the temperature. This law holds good, whether the vapour be pure, or mixed with air or any other gas.

The elasticity of watery vapour at temperatures below 212° was carefully examined by Dalton (Manchester Memoirs, vol. v.); and his results, together with those since published by Ure (Phil. Trans. 1818), are presented in a tabular form at the end of the volume. They were obtained by introducing a portion of water into the vacuum of a common barometer, and estimating the tension of its vapour by the extent to which it depressed the column of mercury at different temperatures.

---

* See a paper by the late Dr. Marcet, in Nicholson's Journal, vol. xxxiv.

A knowledge of the influence of heat and pressure over the volume of gaseous matter is elegantly employed in calculating the sp. gr. of vapour; but before giving the mode of making the calculation, it will be useful to explain what is meant by *specific gravity* or *density*. These terms are generally used to denote the compactness of a substance, or the quantity of ponderable matter contained in a body compared with the space which it occupies. The sp. gr. of a substance is found by dividing its weight by its volume. Thus, if d, w, v, represent the sp. gr. weight and volume of aqueous vapour, and d', w', v', the sp. gr. weight and volume of air, then $d = \frac{w}{v}$, and $d' = \frac{w'}{v'}$. Hence, comparing these sp. gravities, $d : d' :: \frac{w}{v} : \frac{w'}{v'}$; if the volumes are equal, then $d : d' :: w : w'$; and if the weights are equal, $d : d' :: \frac{1}{v} : \frac{1}{v'}$. Consequently, the sp. gravities of substances which have an equal volume are directly as their weights; and when the weights are equal, the sp. gravities are inversely as the volumes. Accordingly, if we weigh an equal volume of any number of substances, temperature and pressure being the same in all, the sp. gr. of each respectively will be represented by its weight. Thus, Gay-Lussac ascertained that if a certain volume of air at 212° and 30 Bar. weigh 1000 grains, an equal volume of aqueous vapour, at the same temperature and pressure, will weigh 625 grains; and, therefore, the sp. gr. of steam is 625 compared to that of air as 1000. Atmospheric air is universally taken as a term of comparison for the sp. gr. of gaseous substances, and pure water for that of liquids and solids.

It admits of inquiry whether liquids of weak volatility, such as mercury and oil of vitriol, give off any vapour at common temperatures. An opinion has prevailed, that evaporation not only takes place from the surface of these and similar liquids at all times, but that vapour of exceedingly weak tension is emitted at common temperatures from all substances however fixed in the fire, even from the earths and metals, when they are either in a vacuum, or surrounded by gaseous matter. It has accordingly been supposed, that the atmosphere contains diffused through it minute quantities of the vapours of all the bodies with which it is in contact; and this idea has been made the basis of a theory of the origin of meteorites. But this doctrine has been successfully combated by Faraday, in his essay On the Existence of a Limit to Vaporization (Phil. Trans. 1826). He has there shown that in many substances the forces of gravity and cohesion are sufficient to overpower elasticity, and that at ordinary temperatures they give off no vapour whatever.

The presence of vapour has a considerable influence over the bulk of gases; and as chemists often determine the quantity of gaseous substances by measure, it is important to estimate the increase of volume due to the presence of moisture. The mode by which a vapour acts is obvious. When two gases, which do not act chemically on each other, are intermingled, each retains the elasticity suited to its volume, exactly as if the other gas were absent; so that the elasticity of the mixture is the sum of the elastic forces of its ingredients. The same remark applies to the mixture of gases and vapours. If a few drops of water are added to a portion of dry air, confined in a glass tube over mercury, the air will speedily become saturated with vapour, and must in consequence be increased in bulk. For the elastic power of the vapour being added to that previously exerted by the gas alone, the mixture will necessarily exert a stronger pressure upon the mercury that confines it, and will therefore occupy a greater space. It is equally clear that the degree of augmentation will depend on the temperature; for it is the temperature alone which determines the elasticity of the vapour.

As the elasticity of vapour is not at all affected by mere admixture with gases, it is easy to correct the fallacy to which its presence gives rise, by means of the data furnished by the experiments of Dalton. The formula for the correction is thus deduced. Let n be the bulk of dry air or other gas expressed in the degrees of a graduated tube; p the elasticity of the dry air, equal to the atmospheric pressure as measured by a barometer; n' the bulk of the air when saturated with watery vapour, and f the elasticity of that vapour (Biot's Traité de Phys. I. 303). Now, as the elasticity of a gas for equal temperatures is inversely as its volume, it follows that when the dry air increases in bulk from n to n', its elasticity will diminish in the ratio of n' to n. Hence its elasticity ceases to be $= p$, and is expressed by $\frac{pn}{n'}$; p is then $= \frac{pn}{n'} + f$; that is, the elasticity of the moist air, added to the elasticity of the vapour present, is equal to the pressure of the atmosphere. From this last equation are deduced the following values: $pn + fn' = pn'$; $pn = pn' - fn'$; and $n = \frac{n'(p-f)}{p}$. One example will suffice for showing the use of this formula. Having 100 measures of air saturated with watery vapour at 60°, the barometer standing at 30 inches, how many measures would the air occupy if quite dry? $n' = 100$; $p = 30$; $f = 0{\cdot}524$, the tension of watery vapour at 60°, according to Dalton's table.* Hence $n = \frac{100 \times (30 - 0{\cdot}524)}{30} = \frac{100 \times 29{\cdot}476}{30} = 98{\cdot}25$, which is the answer required.

The quantity of vapour present in the atmosphere is very variable, in consequence of the continual change of temperature to which the air is subject. But even when the temperature is the same, the quantity of vapour is still found to vary; for the air is not always in a state of saturation. At one time it is excessively dry, at another it is fully saturated; and at other times it varies between these extremes. This variable condition of the atmosphere as to saturation is ascertained by the hygrometer.

A great many hygrometers have been invented; but they may all be referred to three principles. The construction of the first kind of hygrometer is founded on the property possessed by some substances of expanding in a humid atmosphere, owing to a deposition of moisture within them; and of parting with it again to a dry air, and in consequence contracting. Of these, none is better than the human hair, which not only elongates freely from imbibing moisture, but, by reason of its elasticity, recovers its original length on drying. The hygrometer of Saussure is made with this material.

The second kind of hygrometer points out the opposite states of dryness and moisture by the rapidity of evaporation. Water does not evaporate at all when the atmosphere is completely saturated with moisture; and the freedom with which it goes on at other times is in proportion to the dryness of the air. The hygrometric condition of the air may be determined, therefore, by observing the rapidity of evaporation. The most convenient method of doing this is by covering the bulb of a thermometer with a piece of silk or linen, moistening it with water, and exposing it to the air. The descent of the mercury, or the cold produced, will correspond to the quantity of vapour formed in a given time. Leslie's hygrometer is of this kind.

---

* Manchester Memoirs, vol. v.

The third kind of hygrometer is on a principle entirely different from the foregoing. When the air is saturated with vapour, and any colder body is brought into contact with it, deposition of moisture immediately takes place on its surface. The degree indicated by the thermometer when dew begins to be deposited, is called the *dew-point.* If the saturation be complete, the least diminution of temperature is attended with the formation of dew; but if the air is dry, a body must be several degrees colder before moisture is deposited on its surface; and indeed the drier the atmosphere, the greater will be the difference between its temperature and the dew-point. Attempts were made to estimate the hygometric state of the air on this principle by the Florentine Academicians, but the first accurate method was introduced by Le Roi, and since adopted by Dalton. It consists simply in putting cold water into a glass vessel, the outside of which is carefully dried, and marking the temperature of the liquid at which dew begins to be deposited on the glass. The water when necessary is cooled either by means of ice or a freezing mixture. A convenient form of apparatus is a small cup made of thin silver, nicely gilt on the outside, capable of holding about half an ounce of water, and fitted into a case of turned wood lined with cloth, which serves as a stand for the cup during an observation. The water is cooled by successively adding a few grains of a powder made of equal parts of nitre and sal-ammoniac intimately mixed, stirring with the bulb of a small thermometer. As soon as dew is deposited, the temperature is noted; and the first observation is corrected by waiting until the cup and its contents grow warmer, and observing the temperature at which the dew begins to disappear. The last observation is the most trustworthy. This method, when deliberately performed, so that the cup, the solution, and the thermometer should have time to acquire the same temperature, is susceptible of great precision.

The hygrometer of Daniell, described in his Meteorological Essays, acts on the same principle. It consists of a cryophorus, as described at page 51, but modified somewhat in form, and containing ether instead of water. Within one of its balls is fixed a delicate thermometer, the bulb of which is partially immersed in the ether so as to indicate its temperature, and the other ball is covered with muslin. When the instrument is used the muslin is moistened with ether, and the cold produced by its evaporation condenses the vapour within the cryophorus, and causes the ether to evaporate rapidly in the other ball. The cold thus generated chills the ether itself and the ball containing it; and in a short time its temperature descends so low, that dew is deposited on the surface of the glass. As soon as this takes place, the temperature is observed by the thermometer.

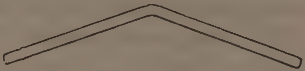
The same object is attained in a still easier way by means of a contrivance described by Jones of London (Phil. Trans. 1826), and soon after by Coldstream of Leith (Phil. Journ. ix. 155). It consists of a delicate mercurial thermometer, the bulb of which is made of thin black glass, and, excepting about a fourth of its surface, is covered with muslin. On moistening the muslin with ether, the temperature of the bulb and mercury falls, and the uncovered portion of the bulb is soon rendered dim by the deposition of moisture. The temperature indicated at that instant by the thermometer is the dew-point.

It is desirable on some occasions, not merely to know the hygrometric condition of air or gases, but also to deprive them entirely of their vapour. This may be done to a great extent by exposing them to intense cold; but the method now generally preferred is by bringing the moist gas in contact with some substance which has a powerful chemical attraction for water. Of these none is preferable to chloride of calcium.

CONSTITUTION OF GASES WITH RESPECT TO HEAT.

From the experiments of Faraday on the liquefaction of gaseous substances, gases may be viewed as the vapours of extremely volatile liquids. Most of these liquids, however, are so volatile, that their boiling point, under the atmospheric pressure, is lower than any natural temperature; and hence they are always found in the gaseous state. By subjecting them to great pressure, their elasticity is so far counteracted that they become liquid. But even when thus compressed, a very moderate heat is sufficient to make them boil; and on the removal of pressure they resume the elastic form, most of them with such violence as to cause a report like an explosion, and others with the appearance of brisk ebullition. Intense cold is produced at the same time, in consequence of their heat passing from a sensible to an insensible state.

The process for condensing gases (Philos. Trans. 1823) consists in exposing them to the pressure of their own atmospheres. The materials for producing the gas are put into a strong glass tube, which is afterwards sealed hermetically, and bent in the middle, as represented by the figure. The gas is generated, if necessary, by the application of heat; and when the pressure becomes sufficiently great, the liquid is formed and collects in the free end of the tube, which is kept cool to facilitate the condensation. Most of these experiments are attended with danger from the bursting of the tubes, against which the operator must protect himself by the use of a mask.



The pressure required to liquefy gases is very variable, as will appear from the following table of the results obtained by Faraday.

Sulphurous acid gas	2	atmospheres at	45°
Sulphureted hydrogen gas	17		50°
Carbonic acid gas	36		32°
Chlorine gas	4		60°
Nitrous oxide gas	50		45°
Cyanogen gas	3·6		45°
Ammoniacal gas	6·5		50°
Muriatic acid gas	40		50°

Additional light has been thrown on the nature of gases by M. Thilorier, who has succeeded in obtaining carbonic acid gas in a solid state (Ann. de Ch. et Ph. lx. 431). It is procured by directing a jet of the liquid carbonic acid into a small glass phial, which is rapidly filled with solid carbonic acid in the form of a white flocculent powder. The solidification is evidently produced by the cold occasioned by the sudden transition of a liquid into a gas, in which state it occupies a space 400 times greater than its original volume. The degree of cold thus produced is estimated by Thilorier at — 148°, at which temperature carbonic acid appears to be entirely deprived of its elastic force; for the solid exposed to the ordinary atmospheric pressure and temperature evaporates slowly and quietly, and is gradually converted into carbonic acid gas.

SOURCES OF HEAT.

The sources of heat may be reduced to six:—1. The sun. 2. Combustion. 3. Electricity. 4. The bodies of animals during life. 5. Chemical action. 6. Mechanical action.—All these means of procuring a supply of heat, except the last, will be more conveniently considered in other parts of the work.

The mechanical method of exciting heat is by friction and percussion. When parts of heavy machinery rub against one another, the heat excited, if the parts of contact are not well greased, is sufficient for kindling wood. The axle-trees of carriages have been burned from this cause, and the sides of ships are said to have taken fire by the rapid descent of the cable. Count Romford has given an interesting account of the heat excited in boring cannon, which was so abundant as to heat a considerable quantity of water to its boiling point. It appeared from his experiments that a body never ceases to give out heat by friction, however long the operation may be continued; and he inferred from this observation that heat cannot be a material substance, but is merely a property of matter. Pictet observed that solids alone produce heat by friction, no elevation of temperature taking place from the mere agitation of fluids with one another. He found that the heat excited by friction is not in proportion to the hardness and elasticity of the bodies employed. On the contrary, a piece of brass rubbed with a piece of cedar wood produced more heat than when rubbed with another piece of metal; and the heat was still greater when two pieces of wood were employed.

SECTION II.

LIGHT.

OPTICS, from *οπτομαι I see*, is the science which treats of light and vision. On the nature of light two rival theories exist, the *undulatory* and *corpuscular*. Prior to and about the time of Newton's celebrated analysis of solar light in 1672, Descartes, Hooke, Huygens, and others, had entertained the former; but Newton, in adopting the latter, led to its almost general reception. He considered light to consist of inconceivably minute particles, too subtile to exhibit the common properties of matter, though really material, which emanate from luminous bodies, such as the sun, the fixed stars, and incandescent substances, travel with immense velocity, and excite the sensation of light by passing bodily through the substance of the eye, and striking against the expanded nerve of vision, the retina. This theory, with which the language of optics has become identified, prevailed with almost no opposition from the time of Newton till 1801, when the undulatory theory was revived and supported with great ability by Young (Phil. Trans.). By the researches of others, the testimony in favour of this doctrine gradually gained ground, and at present it is all but generally adopted. While some phenomena, as the absorption and refraction of light, are even yet obscurely explained by either theory, others, especially the phenomena of interference and polarized light, are wholly inexplicable by the corpuscular, and receive a most lucid explanation by the undulatory theory. On this ground the former is considered untenable, and the latter alone suitable to the present condition of science. But to enter at length into this argument would be so foreign to the design of this treatise, that the reader is referred to Pouillet's *Elémens de Physique*, Young's Essays, Airy's Tracts, 2nd edition, and Herschel's article on Light in the Encyclopedia Metropolitana.

I shall now, however, state the laws of light in the ordinary language, which is founded on the corpuscular theory, and analogous to that which has been employed in treating of heat.

Diffusion of Light.—Light emanates from every visible point of a luminous object, and is equally distributed on all sides if not intercepted, diverging like radii drawn from the centre to the circumference of a circle. Thus, if a single luminous point were placed in the centre of a hollow sphere, every point of its concavity would be illuminated, and equal areas would receive equal quantities of light. The smallest portion of light which can be separated from contiguous portions is called *a ray of light*. Each ray, when not interrupted in its course, and while it remains in the same medium, moves in a straight line; as is obvious by the appearance of shadows cast by the side of a house, or of a sunbeam admitted through a small aperture into a dark room. Owing to these modes of distribution, it follows that the quantity of light which falls upon a given surface decreases as the square of its distance from the luminous object increases, the same law which regulates the heating power of a hot body. (Page 14.)

The passage of light is progressive, time being required for its motion from one place to another. By astronomical observations it is found that light travels at the rate of nearly 195,000 miles in a second of time, and would require about eight minutes to pass from the sun to the earth. Owing to this prodigious velocity, the light caused by the firing of a cannon or a sky-rocket is seen by different spectators at the same instant, whatever may be their respective distances from the rocket, the time required for light to travel 100 or 1000 miles being inappreciable to our senses.

When light falls upon any body, it may, like radiant heat (page 14), dispose of itself in three different ways, being *reflected*, *refracted*, or *absorbed.* The phenomena connected with the two former modes of distribution I shall proceed to consider in succession; while those of absorbed light will be included under the head of *Decomposition of Light.*

REFLECTION OF LIGHT.

Light may be reflected by all media, whether solid, liquid, or gaseous, when it passes from one medium into another of a different nature or density; but there is great difference in the power of reflection. Bright metallic surfaces, such as polished brass and silver, or clean mercury, reflect nearly all the rays which fall upon them; while those which are dull and rough reflect but few. The reflection of light, like that of heat, takes place at the surface of bodies, and appears influenced rather by the condition of the surface than by the nature of the reflecting body. The direction of the reflected ray, whatever may be the nature or figure of the reflecting surface, is regulated by these two laws.

I. The incident and reflected rays always lie in the same plane, which plane is perpendicular to the reflecting surface.

II. The incident and reflected rays always form equal angles with the reflecting surface; or, what amounts to the same, the angle of incidence is always equal to the angle of reflection.

Hence, if the reflecting surface be a plane mirror, the direction of the reflected ray, being known, gives us that of the incident ray; and *vice versâ.*

These laws apply equally to curved reflecting surfaces, whether convex or concave. As a curve may be viewed as a polygon with very short sides, it follows, from obvious mathematical considerations, that parallel rays, falling on a convex mirror, are scattered or made to diverge; while if they fall on a concave mirror they are concentrated, or made to converge into its focus. On the same principle it is plain that divergent rays, falling on a convex surface, are rendered parallel by reflection; and that rays, diverging from the focus of a concave mirror on its surface, are also reflected in parallel lines.

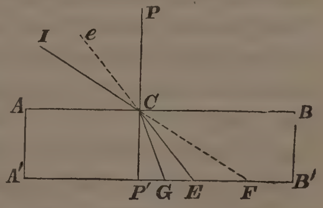
When the concave mirror is spherical, the parallel rays falling on it are not strictly collected into one point or focus; this only happens when the mirror is accurately parabolic. Hence, if a luminous body be placed in the focus of one parabolic reflector, the rays which it gives off are all collected in the focus of a second parabolic reflector placed opposite to the first.

On these principles are constructed the reflecting telescope and the reflecting microscope; but this treatise is not the place for a description of these useful instruments.

REFRACTION OF LIGHT.

Light traverses the same transparent medium, such as air, water, or glass, in a straight line, provided no reflection occurs, and there is no change of density; but when it passes from one medium into another, or from one part of the same medium into another of a different density, a change of direction always ensues at the plane of junction of the media, except when the ray is perpendicular to that plane. For instance, let AB A′B′, fig. 1, represent a vertical section of a vessel full of water, and PP′ the perpendicular to the surface of the water at the point C. Should a ray of light enter the water perpendicularly to its surface, as in the line of PC, it will continue on its course to P′ without deviation; but if it descend obliquely, as in the direction of IC, it will suffer a bend at C, and proceed to E, instead of advancing along the dotted line to F. Conversely, were a ray of light to emanate from E and emerge at C, it would not advance to *e*, but take the direction of CI. By comparing the direction of the refracted ray in these two cases in relation to the vertical PP′, it will be seen that the ray approaches the perpendicular in entering from air into water, and recedes from

Fig. 1.



it in passing out of water into air. The same remark applies to the passage of light from or into air into or out of solid or liquid media in general.

Bodies differ in their power of refracting light. In general, the denser a substance is, the greater is the deviation which it produces. If in fig. 1 sulphuric acid were mixed with the water, the ray IC would be refracted to some point between E and G; and if a solid cake of glass were substituted for that liquid, the refracted ray would be bent down to CG. But this is far from universal:—alcohol, ether, and olive oil, which are lighter than water, have a higher refractive power. Observation has shown it to be a law, to which no exception is yet known, that oils and other highly inflammable bodies, such as hydrogen, diamond, phosphorus, sulphur, amber, olive oil, and camphor, have a refractive power which is from two to seven times greater than that of incombustible substances of equal density. But whatever may be the refractive power of bodies in relation to each other, refraction is always governed by the two following laws, discovered in 1618 by Snell, though usually ascribed to Descartes.

1. The direction of the incident and refracted ray is always in a plane perpendicular to the surface common to the media.

2. The sine of the angle of incidence and the sine of the angle of refraction are in a constant relation for the same media.

The sine of the angle of refraction being taken $=1$, the sines of the angles of incidence in different substances may thus be referred to a common measure or unit of comparison. In common flint glass the ratio is nearly as 1·6 to 1; in water, as 1·336 to 1. The numbers representing the sines of the angles of incidence are called the *indices of refraction*, and indicate the degree of refractive power. Thus, the index of refraction of flint glass is 1·6; that of water, 1·336; that of the diamond, 2·755.

Subjoined is a table of the refractive indices of gases, that of a vacuum being unity.

Name of Gas.	Ref. Index.
Oxygen	1·000272
Hydrogen	1·000138
Nitrogen	1·000300
Chlorine	1·000772
Protoxide of Nitrogen	1·000503
Binoxide of Nitrogen	1·000303
Olefiant Gas	1·000678
Marsh Gas	1·000443
Ether Vapour	1·001530
Carbonic Oxide	1·000340
Carbonic Acid	1·000449
Hydrochloric Acid	1·000449
Ammonia	1·000385
Cyanogen	1·000834
Hydrocyanic Acid	1·000451
Sulphurous Acid	1·000665
Hydrosulphuric Acid	1·000644
Bisulphuret of Carbon Vapour	1·001500

In studying the influence of curved media on light on the same principles as have been applied to reflection by curved mirrors, it is found that convex lenses act like concave mirrors, and collect the refracted rays into a focus; while concave lenses, like convex mirrors, cause the rays to diverge. The properties of convex lenses are, therefore, extensively applied in the construction of the refracting telescope, which is the kind most commonly employed, and of the refracting microscope.

A convex lens fitted into the wall of a darkened chamber constitutes the arrangement of a *camera obscura*, the inverted images of external objects being received on a disk of paper or a white board. In the simple telescope the lens is placed at the extremity of a tube of such length that the image may be formed within the tube, and the observer looks from the other end at the image formed in the air. The eye acts on the same principle. Luminous rays entering the transparent parts of the eye are refracted by the cornea and crystalline lens, and are brought into a focus at the bottom of the eye, an inverted image of external objects being formed upon the retina as on the table of a camera obscura. For distinct vision it is necessary that this image should be formed exactly on the retina. Hence, were the eye an ordinary lens, having an invariable focus, our range of vision would be very narrow; an eye fitted for seeing at a distance would be useless for near objects; and persons who could see near objects would be blind to remote ones. Two rays emanating from a distant point cannot *both* fall upon so small an object as the eye, unless they are nearly parallel; for if they diverged by even a very small angle, they would before reaching the eye separate by an interval exceeding the diameter of the cornea. On the contrary, rays in rapid divergence may enter the eye, provided the point from which they emanate be close to it; and the nearer the object, the more divergent the rays which enter. When, therefore, we observe a distant landscape, then successively notice nearer and nearer objects, and lastly cast the eyes upon the page of a book only six inches distant, we receive rays coming from a multitude of different objects, each set of rays having its own peculiar divergence, and requiring a separate focus; and yet, so wonderful is the adjusting power of the eye, a single minute suffices for distinctly seeing all the objects so beheld, without the consciousness of an effort.

The adjustment of the eye for different distances appears to depend on a power of increasing or decreasing the distance between the posterior part of the eye and the lens; though the mechanism by which this is accomplished is unknown. Some ascribe it to a change in the figure of the whole eye-ball, produced by the muscles which move the eye; but Brewster, I think with better reason, considers the position of the lens to be varied by the same contractile tissue which determines the movements of the iris and the size of the pupil. To this adjusting power, however, there is a limit. The distance at which most persons see small objects distinctly is about six inches: at shorter distances the rays are so divergent, that their focal point falls behind the retina, and indistinct vision is the consequence. Persons called *long-sighted* are unable to see near objects distinctly, owing to a weak refracting power of the eye, due to deficient convexity or density in the humours of the eye. This is the infirmity of advancing life, and is remedied by convex glasses, which cause diverging rays to be parallel or slightly convergent. In *short-sighted* persons the refractive power, either from undue convexity or undue density of the cornea and lens, is so powerful, that all rays which do not diverge rapidly are brought to a focus before they reach the retina. Youth is the period most obnoxious to this imperfection, and assistance is derived from a concave glass, which causes parallel rays to diverge, and thereby counteracts the refracting influence of the eye.

Since the rays which fall on a convex lens from any object are divergent, and are collected into a focus behind the lens, it follows that the image there formed must be inverted, the rays from the top of the object forming the lower part, in point of position of the image. Yet the eye sees objects erect. This remarkable fact has not yet been satisfactorily explained. It has been supposed by some that in infancy we actually see objects inverted, and only discover that they are not so by the correction derived from experience; but this fallacy has been fully corrected by observation on persons born blind, who first obtained the power of vision when of an age to describe what they saw.

Double Refraction.—If on a piece of paper with a black line on its surface we place a rhombohedron of Iceland-spar, and then look at the line through the crystal, it will be found that in a certain position the line appears single as when seen through water or glass; but in other positions of the crystal two lines are visible parallel to each other, and separated by a distinct interval. The light in passing through the crystal is divided into two portions, one of which obeys the laws of refraction already explained (page 62); whereas the other portion proceeds in a wholly different direction, and hence gives the appearance of two objects instead of one. The former is termed the *ordinary*, the latter the *extraordinary* ray. This phenomenon is known by the name of *double refraction*, and has been witnessed in many crystallized substances, as in minerals and artificial salts.

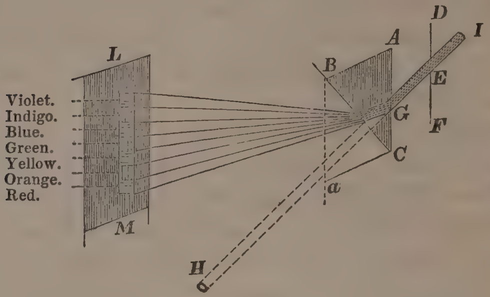
Light transmitted through Iceland-spar or other doubly refracting substances, is found to have suffered a remarkable change. In this state it is distinguished from common light by the circumstance, that when it falls upon a plate of glass at an angle of 56° 11′, it is almost completely reflected in one position of the glass, and is hardly reflected at all in another: if reflected when the plane of reflection is vertical, no reflection ensues when the reflecting plane is horizontal, the incident angle being maintained at 56° 11′. This curious property, so different from common light, has been theoretically ascribed to a kind of *polarity* of such sort, that each side of a ray of light is thought to have a character different from the two adjacent sides at right angles to it; and hence the origin of the term *polarized light*, by which this property is distinguished. Light is polarized by reflection from many substances, such as glass, water, air, ebony, mother-of-pearl, and many crystallized substances, provided the light is incident at a certain angle peculiar to each surface, and which is called the *polarizing angle*. Thus, the polarizing angle for glass is 56° 11′, and for water 53° 14′; that is, common light reflected by glass and water at the angles stated will be polarized.

The phenomena of double refraction and polarized light constitute a department of optics of great and increasing interest; but it is too remote from the pursuits of a chemical student to be treated of at length in this work. Those interested in such studies will find an excellent guide in Brewster's Treatise on Optics in the Cabinet Cyclopedia.

DECOMPOSITION OF LIGHT.

The analysis of light may be effected either by refraction or absorption. Newton, who discovered the compound nature of solar light, effected its decomposition by refraction, employing a solid piece of glass bounded by three plane surfaces, well known under the name of the *prism*. His mode of operating consisted in admitting a ray of light IG, fig. 2, into a dark chamber through a window-shutter DEF, and interposing the prism ACB, so that the

Fig. 2.



ray should pass obliquely through two surfaces, and be refracted by both. On receiving the refracted ray upon a piece of white paper LM, there appeared, instead of a spot of white light, an oblong coloured surface composed of seven different tints, called the *prismatic* or *solar spectrum.* On subjecting each of these colours to refraction no further separation was accomplished; but on causing the rays separated by one prism to pass through a second of the same power and in an inverted position CB*a*, the seven colours disappeared, and a spot of white light appeared at H, in the very position which it would have occupied had both prisms been absent. From such and similar experiments Newton inferred that white light is a mixture of seven *colorific* rays—red, orange, yellow, green, blue, indigo, and violet; and that the separation of these primary or simple rays depended on an original difference of refrangibility, violet being the most refrangible and red the least so.

Though a prism is the most convenient instrument for decomposing light, the separation of the coloured rays is more or less effected by refracting media in general. Lenses, accordingly, disperse the colorific rays at the same time that they refract them; and this effect constitutes one of the greatest difficulties in the construction of telescopes, in so much as the separation or *dispersion*, as it is termed, of these rays diminishes the distinctness of the image. The combinations by which the defect is remedied are called *achromatic.*

Newton's analysis of light led him to explain the origin of the colours of natural objects. Of opaque bodies those are black which absorb all the light that falls upon them, and those white which reflect it unchanged: the various combinations of tints are the consequence of certain rays being absorbed, while those alone whose intermixture produces the observed colour are reflected. The same applies to transparent media, which are colourless like pure water when the light passes through unchanged, but are coloured when some rays are transmitted and others absorbed. This absorption of certain rays by coloured media, such as glass of different tints, affords another mode of decomposing light; and Brewster has ingeniously applied it to analyse the seven colours which compose the prismatic spectrum. He has proved by such experiments, what has been maintained before, that the seven colours of the spectrum are occasioned not by seven, but by three simple or primary rays; namely, the red, yellow, and blue. These rays are concentrated in those parts of the spectrum where each primary colour respectively appears; but each spreads more or less over the whole spectrum, the mixture of red and yellow giving orange, of yellow and blue green, and red with blue and a little yellow causing the violet.

The prismatic colours, according to the experiments of Sir W. Herschel, differ in their illuminating power: the orange illuminates in a higher degree than the red, the yellow than the orange. The maximum of illumination lies in the brightest yellow or palest green. The green itself is almost equally bright with the yellow; but beyond the full deep green the illuminating power sensibly decreases. The blue is nearly equal to the red, the indigo is inferior to the blue, and the violet is the lowest on the scale. (Phil. Trans. 1800.)

Calorific rays in Light.—The solar rays, both direct and diffused, are capable of exciting heat. When reflected or transmitted, no such effect results: the concave reflector and burning-glass remain cool, though intense heat is developed at their foci; and the atmosphere is not heated by the solar rays to which it gives a passage. But opaque bodies which absorb light are invariably heated by it, and the temperature is proportional to the absorbent power. Hence, dark-coloured substances, which are more absorbent than light ones, become hotter when exposed to sunshine. This is attested by the general preference given to light-coloured clothing during summer. Hooke, and subsequently Franklin, proved the fact by exposing pieces of cloth of the same texture and size, but different colours, upon snow to sunshine; when the snow under the dark specimens was found to melt more freely than under the light ones, the effect being nearly proportional to the depth of shade. Davy arrived at similar results. The coloured rays of the spectrum differ in heating power. This is shown generally by looking at the sun through glass of different colours, when it will be found that red and yellow glasses heat and oppress the eye much more than blue or green ones; but the fact was first rigidly demonstrated by Sir W. Herschel, by placing the bulb of a delicate thermometer in the coloured spaces of the solar spectrum. He found that it stood highest in the red space, fell lower and lower when successively removed towards the violet, and was lowest in the violet space. (Phil. Trans. 1800.)

The foregoing facts are explicable on the suppositions either that light is convertible into heat by absorption, or that heat is merely associated with light, and is absorbed along with it. Herschel maintained the latter view, and founded it on his observation that, though the red space of the spectrum is hotter than the other coloured spaces, there is a spot a little beyond the red, where little or no light appears, where the thermometer is higher than in the red itself. He hence inferred that there exists in the solar beam a distinct kind of ray, which causes heat but not light; and that these rays, from being less refrangible than the luminous ones, deviate in a smaller degreee from their original direction in passing through the prism.

All succeeding experimenters confirm the statement of Herschel, that the prismatic colours differ in heating power; but they do not agree as to the spot where the heat is greatest. Englefield, Davy, and others affirmed with Herschel that it is beyond the red ray; while others, and in particular Leslie, contended that it is in the red itself. The observations of Seebeck (Edin. Journ. of Science, i. 358) explained these contradictory statements, by showing that the point of greatest heat varies with the kind of prism which is employed for forming the spectrum. When he used a prism of fine flint-glass, the greatest heat was uniformly beyond the red; with a prism of crown-glass, the red itself was the hottest part; and with a prism externally of glass, but containing water within, the maximum heat was neither in the red itself, nor beyond it, but in the yellow. These experiments have been confirmed by Melloni, who has succeeded with a prism of rock-salt in separating the spot of maximum heat from the coloured part of the spectrum by a much greater interval than had been done previously, and dissipating all remaining doubt as to the existence in solar light of calorific rays distinct from those rays which produce colour. As in simple radiant heat (page 18), there exist in solar light calorific rays of different characters, some being more, some less, refrangible. The former are proportionally less absorbed by feebly diathermanous media than the latter; whereas good diathermanous media absorb the less refrangible more freely than the more refrangible rays. For instance, the heat of the violet passes through water more readily than that of the yellow space, that of the yellow than the red; but in employing media always rising in transcalency, as crown-glass, flint-glass, and rock-salt, the obstruction to the least refrangible calorific rays continually decreases. Hence, in successively taking prisms of rock-salt, flint-glass, crown-glass, and water, the spot of greatest heat will be found first far beyond the red, then nearer the red, then in the red itself, and lastly in the yellow space of the spectrum. On using a prism still less transcalent than water, the maximum heat would be found on the violet side of the yellow space. By causing light, terrestrial as well as solar, to pass first through water, and then through glass coloured green by oxide of copper, Melloni so effectually absorbed all the calorific rays, that the issuing light did not affect the most delicate thermoscope. It would hence follow, not merely that light is associated with calorific rays quite distinct from the luminous rays, but that the latter contributes nothing to the heat evolved during its absorption.

Chemical rays. — Solar light is capable of producing powerful chemical changes. One of the most striking instances of it is its power of darkening the white chloride of silver; an effect which takes place slowly in the diffused light of day, but in the course of two or three minutes by exposure to sunshine. This effect was once attributed to the influence of the luminous rays; but Ritter and Wollaston traced it to the presence of certain rays that excite neither heat nor light, and which, from their peculiar agency, are termed *chemical* rays. The greatest chemical action is exerted just beyond or at the verge of the violet part of the prismatic spectrum; the spot next in energy is the violet itself; and the property gradually diminishes in advancing to the green, beyond which it seems wholly wanting. It hence follows that the chemical rays are still more refrangible than the luminous, in consequence of which they are dispersed in part over the blue, indigo, and violet, but in the greatest quantity at the extreme border of the latter.

The Daguerréotype, as well as Mr. Talbot's method of Photography, is founded on the action of the chemical rays on certain substances. The iodide of silver, formed by exposing a plate of silver to the vapour of iodine, is the substance used in the Daguerréotype. The chloride, iodide, and bromide of silver, formed on the surface of paper in a thin and uniform layer, are the bases of Talbot's method. The delicacy and beauty of the images produced in the Daguerréotype, however, far surpasses anything that has hitherto been produced on paper. For details on this subject, the student is referred to a little treatise by M. Arago, which has been translated into English.

Magnetizing rays. — The more refrangible rays of light were once thought to possess the property of rendering steel and iron magnetic; but since the experiments of Riess and Moser, this notion has been abandoned. (Brewster's Journal, II. 225.)

TERRESTRIAL LIGHT.

Under this head is included all kinds of artificial light. The common method of obtaining such light is by the combustion of inflammable matter, which gives out so much heat that the burning substance is rendered luminous in the act of being burned. All bodies begin to emit light when heat is accumulated within them in great quantity; and the appearance of glowing or shining, which they then assume, is called *incandescence*. The temperature at which solids in general begin to shine in the dark is between 600° and 700°; but they do not appear luminous in broad daylight till they are heated to about 1000°. The colour of incandescent bodies varies with the intensity of the heat. The first degree of luminousness is an obscure red. As the heat augments, the redness becomes more and more vivid, till at last it acquires a full red glow. If the temperature still increase, the character of the glow changes, and by degrees it becomes white, shining with increasing brilliancy as the heat augments. Liquids and gases likewise become incandescent when strongly heated; but a very high temperature is required to render a gas luminous, more than is sufficient for heating a solid body even to whiteness. The different kinds of flame, as of the fire, candles, and gas light, are instances of incandescent gaseous matter.

Artificial lights differ in colour, and accordingly exhibit different appearances when transmitted through a prism. The white light of incandescent charcoal, which is the principal source of the light from candles, oils, and the illuminating gases, contains the three primary calorific rays, the red, yellow, and blue. The dazzling light emitted by lime intensely heated, first proposed by Lieut. Drummond for the trigonometrical survey (Phil. Trans. 1830), and of late so successfully applied by Messrs. Cooper and Carey for their gas microscope, gives the prismatic colours almost as bright as in the solar spectrum. The light emitted by iron feebly incandescent consists principally of the red rays, as does the red light obtained by means of strontia and lithia; that from ignited boracic acid is such a mixture of the blue and yellow rays as constitutes green; and incandescent soda emits a yellow light almost wholly free from the rays which cause the red and blue colours.

Artificial light differs from solar light in containing heat in two states. It contains simple radiant heat like that radiated from a body not luminous, and which may be separated by transmission through a plate of moderately thick glass; but the light so purified still heats any body which absorbs it, possessing calorific rays associated with its luminous rays like those in solar light (page 67), and like them susceptible of refraction by transparent media. Thus, Daniell found that the rays from incandescent lime were concentrated by convex lenses, and set fire to phosphorus placed in the focus (Phil. Mag. N. S. II. 59). Agreeably to the researches of Melloni (page 19), artificial light contains different modifications of radiant heat, which not only differ in refrangibility, but in transmissibility through diathermanous media.

The chemical agency of artificial light is analogous to that from the sun. In general the former is too feeble for producing any visible effect; but light of considerable intensity, such as that from ignited lime, darkens chloride of silver, and seems capable of exerting the same chemical agencies as solar light, though in a degree proportionate to its inferior brilliancy. (An. of Phil. XXVII. 451.)

Light emanates from some substances either at common temperatures or at a degree of heat disproportioned to the effect, giving rise to an appearance which is called *phosphorescence*. This is exemplified by a composition termed *Canton's phosphorus*, made by mixing three parts of calcined oyster-shells with one of the flowers of sulphur, and exposing the mixture for an hour to a strong heat in a covered crucible. The same property is possessed by chloride of calcium (Homberg's phosphorus), anhydrous nitrate of lime (Baldwin's phosphorus), some carbonates and sulphates of baryta, strontia, and lime, the diamond, some varieties of fluor-spar called *chlorophane*, apatite, boracic acid, borax, sulphate of potassa, sea-salt, and by many other substances. Scarcely any of these phosphori act unless they have been previously exposed to light, though they do not always shine with light of the same colour as that which excites the phosphorescence: for some, diffused daylight or even lamp-light will suffice; while others require the direct solar light, or the light of an electric discharge. Exposure for a few seconds to sunshine enables Canton's phosphorus to shine in a dark room for several hours afterwards. Warmth increases the intensity of light, or will renew it after it has ceased;—but it diminishes the duration. When the phosphorescence has ceased it may be restored, and in general for any number of times, by renewed exposure to sunshine; and the same effect may be produced by passing electric discharges through the phosphorus. Some phosphori, as apatite and chlorophane, do not shine until they are gently heated; and yet if exposed to a red heat, they lose the property so entirely that exposure to solar light does not restore it. Pearsall has remarked that in these minerals the phosphorescence, destroyed by heat, is restored by electric discharges; that specimens of fluor-spar, not naturally phosphorescent, may be rendered so by electricity; and that this agent exalts the energy of natural phosphori in a very remarkable degree. (R. Inst. Journal, N. S. I.) The theory of these phenomena is obscure. Chemical action is not the cause, for these phosphori shine *in vacuo* or in gases which do not act chemically on them, and some even under water. It may be presumed that light causes in them a certain vibratory state analogous to that, though in a far lower degree, which exists in incandescent matter.

Another kind of phosphorescence is observable in some bodies when strongly heated. A piece of lime, for example, heated to a degree which would only make other bodies red, emit sa brilliant white light of such intensity that the eye cannot support its impression.

A third species of phosphorescence is observed in the bodies of some animals, either in the dead or living state. Some marine animals, and particularly fish, possess it in a remarkable degree. It may be witnessed in the body of the herring, which begins to phosphoresce a day or two after death, and before any visible sign of putrefaction has set in. Sea-water is capable of dissolving the luminous matter; and it is probably from this cause that the waters of the ocean sometimes appear luminous at night when agitated. This appearance is also ascribed to the presence of certain animalcules, which, like the glow-worm of this country, or the fire-fly of the West Indies, are naturally phophorescent.

Light sometimes appears during the process of crystallization. This is exemplified by a tepid solution of sulphate of potassa in the act of crystallizing; and it has been likewise witnessed under similar circumstances in a solution of fluoride of sodium and nitrate of strontia. Another instance of the kind is afforded by the sublimation of benzoic acid. Allied to this phenomenon is the phosphorescence which attends the sudden contraction of porous substances. Thus, on decomposing by heat the hydrates of zirconia, peroxide of iron, and green oxide of chromium, the dissipation of the water is followed by a sudden increase of density suited to the changed state of the oxide, and a vivid glow appears at the same instant. The essential conditions are, that a substance should be naturally denser after decomposition than it was previously, and that the transition from one mechanical state to the other should be abrupt.

Instruments designed for measuring intensities of light are termed *photometers*. That of Leslie is the only one used to estimate the strength of the sun's light. It consists of his differential thermometer, with one ball made of black glass. The clear ball transmits all the light that falls upon it, and therefore its temperature is not affected; it is all absorbed, on the contrary, by the black ball, and by heating and expanding the air within, causes the liquid to ascend in the opposite stem. The whole instrument is covered with a case of thin glass, the object of which is to prevent the balls from being affected by currents of cold air. The action of this photometer depends on the absorption of the heat by which light is accompanied.

Leslie recommended his photometer also for determining the relative intensities of artificial light, such as that of candles, oil, or gas. This application of it differs from the foregoing, because light from terrestrial sources contains calorific rays of different properties; some being largely absorbed by glass, and others freely transmissible. The former, being for the most part arrested by the outer glass-case, will not cause any great error; but the latter must give rise to serious fallacies whenever the calorific and luminous rays of the two lights are not in the same ratio. This is rarely, if ever, the case with lights which differ in colour. Thus, the light emitted by burning cinders or red-hot iron, even after passing through glass, contains a quantity of calorific rays, which is out of all proportion to the luminous ones; and, consequently, they may and do produce a greater effect on the photometer than some lights whose illuminating powers are far stronger.

A photometer on a different principle has been described by Rumford in his Essays. It determines the relative strength of lights by a comparison of their shadows, and is susceptible of great accuracy when employed with the required care; but,* like the foregoing, its indications cannot be trusted when there is much difference in the colour of the lights. In this case, the best procedure is, to observe the distance from each light at which any given object, as a printed page, ceases to be distinctly visible. The illuminating power of the lights so compared is as the squares of their distances.

ON THE RELATIONS OF HEAT AND LIGHT.

Radiant heat and light have the most intimate resemblance. They are distributed, reflected, refracted, absorbed, transmitted, polarized, according to laws so exactly parallel, as to force on the mind the conviction that their causes are likewise similar. If light be due to ethereal vibrations, it is difficult not to assign a similar cause to radiant heat. The obstacle to adopting this view arises from the peculiar relations of heat to matter as connected with change of form, with specific heat, and with heat of temperature. The outline of such an undulatory theory might be thus stated:—Heat may be considered identical with the universal ether, so that the terms ether and matter of heat would apply to the same substance. Diffused within the pores of bodies this ether causes the condition of temperature, and in a state of more intimate union it determines their form. Conduction may be due to a peculiar vibration of ether, advancing slowly among the molecules of matter, and modified by their presence,—a radiation from particle to particle. Common radiation of heat may be ascribed, not to the ether itself being ejected from a hot body, but to ethereal impulses originating in the same manner as those of light, but having waves of different grades both of length and intensity. It would not be prudent, however, at present to embody such a theory with the ordinary doctrines of heat, though as a scientific speculation it is a subject of great and increasing interest

---

* See an Essay on the Construction of Coal Gas Burners, &c. in the Edinburgh Philosophical Journal for 1825.

SECTION III.

ELECTRICITY.

Elementary Facts.—When certain substances, such as amber, glass, sealing-wax, sulphur, are rubbed with dry silk or cloth, they are found to have acquired a property, not observable in their ordinary state, of causing contiguous light bodies to move towards them; or if the substances so rubbed be light and freely suspended, they will move towards contiguous bodies. After a while this curious phenomenon ceases; but it may be renewed an indefinite number of times by friction. The principle thus called into action is known by the name of *electricity*, from the Greek word ηλεκτρον, amber, because the electric property was first noticed in it. The same term is applied to the science which treats of the phenomena of electricity.

When a substance by friction or any other means acquires the property just stated, it is said to be *electrified*, or to be *electrically excited;* and its motion towards other bodies, or of other bodies towards it, is ascribed to a force called *electric attraction.* But its influence, on examination, will be found to be not merely attractive; on the contrary, light substances, after touching the electrified body, will be disposed to *recede* from it just as actively as they approached it before contact. This is termed *electric repulsion.* By aid of the electrical machine, electric attraction and repulsion may be displayed by a great variety of amusing and instructive experiments, showing how readily an invisible power is called into operation, and how wonderfully inert matter is subject to its control. But the student may witness these effects quite satisfactorily by very simple apparatus. Let him suspend a thread of white sewing silk from the back of a chair so that one end may hang freely, taking the precaution to moisten that end slightly by holding it between the fingers, while the rest of the thread is carefully dried by the fire; and let him then place near the free end of a piece of sealing-wax previously rubbed on the sleeve of his coat. The silk will move towards it; but after touching the excited wax two or three times, it will recede from it.

When an electrified body touches another which is not electrified, the electric property is imparted by the former to the latter.

Thus, on touching the free end of the suspended silk thread with the excited wax, the silk will itself be excited, as shown by its moving towards a book, a knife, or other unexcited object placed near it. But although electricity is always imparted by an excited to an unexcited body by contact, the latter does not always exhibit electric excitement. If, for example, the suspended silk be wetted along its whole length, it will be strongly attracted by the excited wax, but after contact it will not evince the least sign of being itself electrified. Nevertheless, electricity is communicated to the silk in both cases; only it is retained by silk when dry, and is lost as soon as received by wet silk. Such observations led to the discovery that electricity passes with great ease over the surface of some substances, and with difficulty over that of others, and hence to the division of bodies into *conductors* and *non-conductors* of electricity. If electricity be imparted to one end of a conductor, such as a copper wire, the other extremity of which touches the ground, or is held by a person standing on the ground, the electricity will pass along its whole length and escape in an instant, though the wire were several miles long; whereas excited glass and resin, which are non-conductors, may be freely handled without losing any electricity except at the parts actually touched. To the class of conductors belong the metals, charcoal, plumbago, water, and aqueous solutions, and substances generally which are moist or contain water in its liquid state, such as animals and plants, and the surface of the earth. These, however, differ in their conducting power: of the metals, Harris found silver and copper to be the best conductors; and after these follow gold, zinc, platinum, iron, tin, lead, antimony, and bismuth (Phil. Trans. 1827). This order, as Forbes has remarked, is nearly that of their conducting powers for heat. Aqueous solutions of acids and salts conduct much better than pure water. To the list of non-conductors belong glass, resins, sulphur, diamond, dried wood, precious stones, earth and most rocks when quite dry, silk, hair, and wool. Air and gases in general are non-conductors if dry, but act as conductors when saturated with moisture.

This knowledge is of continual application in electrical experiments. When it is wished to collect electricity on a metallic surface, the metal must be *insulated*, that is, cut off from contact with the earth, and with conductors touching the ground, by means of some non-conductor; an object commonly effected either by supporting it on a handle of glass, or by placing it on a stool made with glass feet. Another mode of insulating is to suspend a substance by silk threads. But such insulators must be dry; since they begin to conduct as soon as they grow damp, and conduct well, as in the experiment above described, when wet. Again, electrical experiments are very apt to fail in damp weather, because the moisture both carries off electricity directly, and by being deposited on the glass supports destroys the insulation.

To diminish this inconvenience it is usual to keep the insulators warm, and to coat them with a varnish made by dissolving the resin called shell-lac in alcohol, this resinous matter being much less prone to attract moisture from the air than glass. The same principles account for an error once prevalent that a metal cannot be excited by friction: if held in the hand, indeed, it exhibits no sign of excitement when rubbed, because the electricity is carried off as soon as excited; but if, while carefully insulated, it is rubbed with a dry cat's fur, excitement readily ensues.

On comparing the electric properties manifested by glass and sealing-wax when both are rubbed by a woollen or silk cloth, they will be found essentially different; hence it is inferred that there are two kinds or states of electricity, one termed *vitreous*, because developed on glass, and the other *resinous* electricity, from being first noticed on resinous substances. These two kinds of electricity, one or other of which is possessed by every electrified substance, are also termed *positive* and *negative*, the terms *vitreous* and *positive* being used synonymously, as are *resinous* and *negative:* they are also denoted by the signs + and —. If two electrified substances are both possitive or +, or both negative or —, they are invariably disposed to recede from each other, that is, to exhibit electric repulsion; but if one be +, and the other —, their mutual action is as constantly attractive. The end of a silk thread, after contact with an electrified stick of sealing-wax, is repelled by the wax, because both are —; but a dry warm wine-glass, if rubbed with cloth or silk, will be +, and if then presented to the thread, attraction will ensue. A silk thread in a *known* electric state, thus indicates the kind of electricity possessed by other substances: a convenient mode of doing this, is to draw a thread of white silk rapidly through a fold of course brown paper previously warmed, by which means its whole length will be rendered +.

When two substances are rubbed together so as to electrify one of them, the other, if in a state to retain electricity, will be excited also, one being always —, and the other +. It is easy to be satisfied of this by very simple experiments. Rub a stick of sealing-wax on warm coarse brown paper, and the paper will be found to repel a positively excited thread of silk, while the wax will attract it ; if a warm wine-glass be rubbed on the brown paper, the glass will be +, as shown by its repelling the + thread, while the same thread will be attracted by the − paper ; friction of sealing-wax on a silk riband renders the wax − and the riband +, but with glass the riband is −. If two silk ribands, one white and the other black, be made quite warm, placed in contact, and then drawn quickly through the closed fingers, they will be found on separation to be highly attractive to each other, the white being +, and the black −. The back of a cat is + to all substances with which it has been tried, and smooth glass is + to all except the back of a cat. Sealing-wax is − to all the substances just enumerated, but becomes + by friction with most of the metals. The reader will perceive from these facts that the same substance may acquire both kinds of electricity, becoming + by friction with one body, and − with another.

THEORIES OF ELECTRICITY.

The nature of electricity, like that of heat, is at present involved in obscurity. Both these principles, if really material, are so light, subtile, and diffusive, that it has hitherto been found impossible to recognise in them the ordinary characteristics of matter ; and therefore electric phenomena may be referred, not to the agency of a specific substance, but to some property or state of common matter, just as sound and light are produced by a vibrating medium. But the effects of electricity are so similar to those of a mechanical agent—it appears so distinctly to emanate from substances which contain it in excess, and rends asunder all obstacles in its course so exactly like a body in rapid motion, that the impression of its existence as a distinct material substance *sui generis* forces itself irresistibly on the mind. All nations, accordingly, have spontaneously concurred in regarding electricity as a material principle ; and scientific men give a preference to the same view, because it offers an easy explanation of phenomena, and suggests a natural language easily intelligible to all.

Theory of two Electric Fluids.—This theory, the fundamental facts of which were supplied partly by Dufay, and partly by Symmer, is founded on the assumed existence of two electric fluids, which Dufay distinguished by the terms *vitreous* and *resinous* electricity. In order to account for electric phenomena by this supposition, the two fluids are assumed to possess the following properties:—They are both equally subtile and elastic, universally diffused and therefore present in all bodies, possessed of the most perfect fluidity, each highly repulsive to its own particles, and as highly attractive to those of the opposite kind, these attractive and repulsive forces being exactly equal at the same distance, and both varying inversely as the square of the distance varies. Electric quiescence is ascribed to these fluids being combined and neutralized with each other; and electric excitation is the consequence of either fluid being in excess. Their combination is destroyed by several causes, of which friction is one.

This theory, as commonly stated, takes little or no cognizance of any attraction between the electric fluids and other material substances. But it would be against all analogy to suppose no such influence to exist; and indeed the supposition of an attractive force acting at insensible distances seems necessary to account for the impediment caused by non-conductors to the free movement of the electric fluids.

Theory of a single Fluid.—The celebrated American philosopher, Franklin, proposed a different theory, founded on the supposition of a single electric fluid, the particles of which are conceived to repel each other with a force diminishing as the squares of the distance, and to be attracted by matter in general according to the same law. Material substance in its unelectric state is regarded as a compound of electricity and matter, saturated and neutralized with each other. It is also an assumption, shown to be necessary by Æpinus and Cavendish, that ponderable bodies repel each other with the same force and according to the same law as the particles of electricity. From the nature of these postulates it will be easy to anticipate their application. Unelectric bodies are such as have their natural quantity of electricity, which precisely suffices to saturate and neutralize the matter of which they consist. They are then electrically indifferent; because the repulsion exerted between the electricity and matter of contiguous bodies is exactly counteracted by the attraction of the electric fluid in each for the matter of the other. Electrical excitement is occasioned either by increase or diminution of the natural quantity of electricity. These opposite states are denoted by the algebraic terms *positive* and *negative;* the former corresponding to the vitreous, the latter to the resinous electricity of Dufay.

To the theory of Franklin it is usually objected that it involves an assumption at variance with the laws of gravitation, namely, that of matter being repulsive to itself; but this objection is unfounded, as the laws of gravitation have been investigated for matter only when in its ordinary state, and probably do not apply in cases of electric excitement. The researches of Mossotti on the forces which regulate the internal constitution of bodies amply justify this conclusion. Adopting with Franklin a single electric fluid, he has shown that gravitation is perfectly consistent with the supposition that the molecules of matter are repulsive to each other. He has supported this opinion by a mathematical investigation of the conditions of equilibrium both for the molecules of matter and for the electric fluid. The results at which he arrived show that two molecules of matter surrounded by their electric atmospheres, are mutually attractive when separated by a sensible distance;—that the attraction increases on the approach of the atoms up to a certain point, where the attractive force attains its maximum, and beyond which the molecules are mutually repulsive. In this manner, gravitation, cohesion, and the resistance of matter to compression, are attributed to the same forces. These views certainly afford a happy explanation of the molecular mechanism; but as they have not yet been sufficiently tested, I shall retain the theory of the two electricities, which was adopted in former editions, substituting however, agreeably to present usage, the terms positive and negative, for vitreous and resinous electricity.

CAUSES OF ELECTRIC EXCITEMENT.

Friction.—This cause of electric excitement having been already mentioned, it here only remains to state the usual modes of developing electricity by friction. A supply of negative electricity is easily obtained by rubbing a stick of sealing-wax, or a glass tube covered with sealing-wax, with silk or woollen cloth; and positive electricity is freely developed when a dry glass tube is rubbed with silk, brown paper, or flannel, the surface of which is covered with a little amalgam. But for obtaining an abundant supply of electricity it is necessary to employ an electrical machine, which is a mechanical contrivance for exposing a large surface of glass to continuous friction. As now constructed, it is formed either with a cylinder or plate of glass which is made to revolve upon an axis, and pressed during rotation by cushions or rubbers made of leather stuffed with flannel, and covered usually with silk. On the rubber is spread an amalgam of tin and zinc, rendered adhesive by admixture with a small quantity of lard or tallow. To prepare the amalgam, melt in a Hessian crucible one ounce of tin and three of zinc, then add two ounces of mercury heated to near its boiling point, stir briskly with a stick for a few minutes, and pour the mixture on a clean dry stone: when cold, pulverize and sift, and preserve the fine powder in a well-corked dry phial. Another essential part of the machine is the *prime conductor*, which is an insulated conductor, commonly made of brass, placed in such immediate proximity to the revolving glass, that the electric state of the one is instantly imparted to the other.

The electricity developed by the electrical machine is due partly to friction, which disunites the combined electric fluids of the glass and rubber, but principally to the oxidation of the amalgam. The positive fluid accumulates in the glass and passes from it to the prime conductor, while the negative fluid accumulates in the rubber, and its conductor. But to keep up the supply of electricity, the rubber must be connected with the ground, so that its − fluid may escape; or if we wish to obtain − electricity from the rubber, the prime conductor should communicate with the ground, that its + fluid may escape.

Change of temperature.—The operation of this cause of electric excitement was first noticed in certain minerals, such as tourmalin and boracite, not possessed of that symmetric arrangement of parts commonly observed in crystals, and which are electrified by the application of heat. But a far more general principle was detected by Seebeck, who found that the electric equilibrium is disturbed in certain metallic rods or wires when one extremity has a different temperature from that of the other, whether the difference be effected by the application of heat or cold. This observation has been since shown by Cumming to be true of all metals (An. of Phil. N. S. v. 427); and the same subject has been examined by Prideaux (Phil. Mag. and An. iii.). The experiment is usually made by heating or cooling the point of junction of two metallic wires, which are soldered together; but Becquerel has proved that the contact of different metals is not essential. (An. de Ch. et Ph. xli. 353.)

Chemical action.—Another, and perhaps by far the most fertile, source of electricity is chemical action. This was strongly denied by Davy, in his Bakerian lecture for 1826; but the experiments of Becquerel, De la Rive, and Pouillet, afford decisive proof that chemical union and decomposition are both attended with electrical excitement (An. de Ch. et Ph. vol. 35, 36, 37, 38, and 39).

Contact.—Another reputed source of electricity is contact of different substances, especially of metals; a source originally suggested by Volta, who founded on it a theory of galvanism. Volta stated that clean plates of zinc and copper, insulated by glass handles, became electric by being made to touch each other, and then separated. When the zinc alone was insulated, it became +, and when the copper alone was insulated, it became −. But the quantity of electricity thus developed is confessedly so small as to require the most delicate instruments to detect it; and the experiments of De la Rive (An. de Ch. et Ph. xxxix. 297; lxii. 147,) and those of Parrot (ibid. xlvi. 361), have shown, in a manner apparently decisive, that the electricity developed in such experiments is derived either from a slight degree of chemical action, or from friction; and that contact alone, if unattended by chemical action or by friction, produces not the least excitement of electricity. I apprehend, therefore, that the facts adduced by Volta must be rejected.

Changes of form.—The changes of form caused in a substance by variations of temperature, such as liquefaction and solidification, the formation and condensation of vapour, constitute another reputed source of electricity. Pouillet, however, questions this opinion; and maintains, that in every case where change of form produces electric excitement, there is also chemical action. Thus, when water evaporates, the electricity is due to the separation of the water from its saline impregnations, or to its action on the containing vessel; and pure water, evaporated in platinum vessels, produces no excitement. He ascribes to the separation of water from saline matter, constantly going on at the surface of the earth, and to the chemical changes produced in the growth of vegetables, the developement of a great part of the atmospheric electricity. My own experiments have given similar results; but Harris, with an apparatus of great delicacy, has detected electricity during the evaporation of pure water in platinum vessels, although in very small quantity.

Proximity to an electrified body.—It is a direct consequence of the attractive and repulsive powers ascribed to the electric fluids, that an unelectrified conductor must be excited by the vicinity of an electrified body. The opposite ends of the conductor are oppositely electrified, and in an equal degree: the excitement is found, as would be anticipated, to be greatest at the extremities, and to diminish gradually towards the middle line, which is neutral. The electricity thus developed by the contiguity of an electrified body is said to be *induced*, or to be excited by *induction*.

The student should reflect carefully on these inferences from the theory of electricity, since the applications of such knowledge are numerous. A few of these may now be enumerated:—

1. An electrified body attracts light objects near it, because it induces in them a state opposite to itself. The attraction is most lively when the light object is a conductor, and in contact with the ground, since it then more completely assumes an electric state opposed to that of the inducing body. A non-conductor is very imperfectly electrified by induction, because the electric fluids cannot quit each other from inability to move through the non-conductor.

2. If a stick of sealing-wax, strongly — be presented to a thread or pith ball which is also negatively, but feebly, excited, repulsion will ensue at a considerable distance, followed by attraction when the distance is small. This attraction is due to the strongly excited wax acting by induction on the feebly — thread, thereby causing it to have an excess of + electricity.

3. The + electricity collected on the prime conductor of an electrical machine is by some ascribed, not to a transfer of that fluid from the glass to the prime conductor, but to a part of the combined electricities of the prime conductor being separated by induction, and the — fluid being imparted to the + glass. The same view is applicable to any system of conductors in contact with the prime conductor, as also to conductors connected with the rubber. It is difficult to say which explanation is the more correct, or whether both may not be true.

4. On moving the hand towards the prime conductor of an excited electrical machine, the hand becomes — by induction, and the spark ultimately obtained restores the equilibrium. In like manner a negatively electrified cloud renders + a contiguous tree or tower, and then a stroke of lightning follows as a consequence of attraction between the two accumulated fluids.

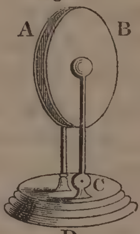
5. The action of the *Leyden jar* depends on the principle of induced electricity. A glass jar or bottle with a wide mouth is coated externally and internally with tinfoil, except to within three or four inches of its summit; and its aperture is closed by dry

wood or some imperfect conductor, through the centre of which passes a metallic rod communicating with the tinfoil on the inside of the jar. On placing the metallic rod in contact with the prime conductor of an excited electrical machine, while the outer coating communicates with the ground, the interior of the jar acquires a charge of + electricity, and the exterior becomes as strongly — . The exterior may be handled without destroying the charge, provided no communication be at the same time made with the interior. But when a conductor communicates with both surfaces at the same instant, the two fluids rush together with violence, and the equilibrium is restored. Whether in this and similar cases the two fluids coalesce entirely on the intermediate conductor, or whether each from its velocity may not in part pass the other, and be projected to the opposite surface, is a question on which electricians are not agreed.

The Leyden jar affords the means of passing through bodies a large quantity of electricity. For not only may jars of any required size be employed, but it is easy so to arrange any number of such jars, that they shall all be charged and discharged at the same time, constituting what is termed an *electrical battery*. The arrangement is made by placing a number of Leyden jars in a box lined with tinfoil, by which means their outer surfaces have free metallic communication with each other, and connecting their inner surfaces by wires.

6. The principle of induced electricity was ingeniously applied by Volta in the construction of the *Condenser*. This apparatus, fig. 1, consists of two brass plates, A and B, supported on a common stand D. One of the plates B is attached to the stand by means of a hinge C, so that, though represented upright, it may be placed horizontally, and be thus withdrawn from the vicinity of the plate A, the support of which is made of glass. On electrifying the insulated plate positively, the plate B, expressly placed close to A, is rendered — by induction; and, as happens in the Leyden jar, the excitement of B will be proportional to that of A. The — charge of B tends to preserve the + charge of A, which may consequently receive still more electricity by contact with any + surface, without losing what it had previously acquired. Thus is electricity accumulated or *condensed* on A; so that a substance too feebly excited to produce any appreciable

Fig. 1.



effects of itself, may by repeated contact with the insulated plate of a condenser communicate a charge of considerable intensity. The effect of the accumulation is made apparent by withdrawing B, and bringing A in contact with a delicate electrometer. The condenser is much employed in experiments of delicacy, and the plate A is often permanently fixed on the gold leaf electrometer.

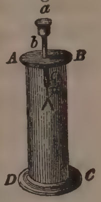
7. The *Electrophorus* is another contrivance of Volta's, which acts by induced electricity. It consists essentially of two parts; one being a flat cake of resin, made by pouring melted resin into a shallow plate or circular dish of tinned iron, and the other a disk of brass, of rather smaller diameter than the resin, supplied with a glass handle. The surface of the resin is negatively excited by friction or flapping with silk or flannel, and the brass disk is laid upon it. The resin being a non-conductor retains its own electricity in spite of the super-imposed brass, and decomposes the combined electricities of the latter, causing its under surface to be +, and its upper −. On touching the brass with the finger, its upper surface is neutralized; and on then withdrawing the brass plate, it is found to have an excess of + electricity. On replacing the brass as before, the resin, having lost none of its electricity in the process, acts again upon the metallic disk as on the first occasion, and will continue so to act for an indefinite number of times. Kept in a dry place, the electrophorus will keep in action for months.

ELECTROSCOPES AND ELECTROMETERS.

It is very important, in experiments on electricity, to possess easy methods of discovering when a substance is electrified, of ascertaining its *intensity* or the degree to which it is excited, and distinguishing the kind of excitement. The means for effecting these objects are founded on electrical attraction and repulsion, and the instruments employed for the purpose are called *Electroscopes* and *Electrometers;* the latter denoting the intensity of electricity,—the former merely indicating excitement, and the electrical state by which it is produced. The term electrometer, however, is often indiscriminately applied to all such instruments, since the methods of ascertaining the kind of excitement give at the same time some idea of its intensity.

Gold Leaf Electrometer.— Several simple electroscopic methods have already been indicated (page 77). Small balls made of the pith of elder are used for the same purpose. A single pith ball, suspended by a cotton thread, is attracted by a feebly electrified substance. Also, when two pith balls are suspended from the same point by cotton threads of equal length, and an electrified body is placed near them, the two balls are thrown by induction into the same electric state, and diverge. The gold leaf electrometer, figure 2, invented by Bennett, acts upon the same principle, but is far more delicate. It consists of a glass cylinder cemented below upon a brass plate CD, and covered above by a brass plate AB, pierced in its centre for the insertion of a glass tube *bc*, the top of which is closed by a brass plate *a*: into this plate is screwed a thick brass wire, which passes through the glass tube, and from the lower end *d* of which two slips of gold leaf are suspended. These different parts are put together while quite dry, all the joinings are secured by wax cement, and the glass is covered by lac varnish. The effect of these arrangements is to insulate the plate *a* with its wire and gold leaves, while the latter are secure against being moved by currents of air. The approach of any electrified body, even though feebly excited, to the plate *a*, is immediately detected by the divergence of the leaves, as shown in the figure. The instrument is equally useful in indicating the kind of excitement, provided the plate and leaves be permanently electrified, which may easily be done on the same principle as in charging the metallic disk of an electrophorus. If the plate be thus charged with + electricity, the leaves diverge, and continue divergent for some time if the air be dry. In this state, the approach of a body charged with + electricity increases the divergence; while the approach of a body charged with − electricity has a contrary effect.

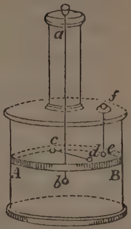
Fig. 2.



Quadrant Electrometer.—An instrument much used for estimating the degree or intensity of electricity is the *quadrant electrometer*, invented by Henley. This instrument, though convenient for experiments of illustration, is not suited to those of research, wherein the object is to examine the effects of substances feebly electrified, and ascertain their relative forces with accuracy.

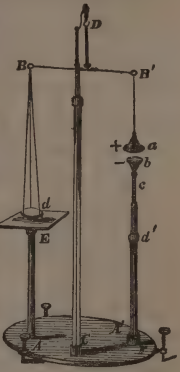
Torsion Electrometer.—This instrument, invented by Coulomb, is peculiarly fitted for scientific investigation. It consists of a small needle of gum-lac *c d*, fig. 3, suspended horizontally by a silk thread as spun by the silkworm, or by a fine silver wire *a b*; on the point of the needle is fixed a small gilt ball made of the pith of elder; and the whole is covered with a glasscase to protect it from moisture and currents of air. The pith ball, when

Fig. 3.



the apparatus is at rest, is in contact with the knob *e* of a metallic conductor *fe*, which passes through a hole in the glass case, and is secured in its place by cement; but when an excited body is made to touch the conductor, the pith ball in contact with it is similarly excited, and recedes from it to an extent proportional to the degree of excitement. The needle consequently describes the arc of a circle, which is measured on the graduated arc AB, and in its revolution twists the supporting thread more or less according to the length of the arc described. The torsion thus occasioned calls into play the elasticity of the thread,—a feeble but constant force, which opposes the movement of the needle, measures by the extent to which it is overcome the repulsive force exerted, and brings back the needle to its original position as soon as the electric equilibrium is restored. It has been proved that the force which causes the torsion is exactly proportional to the arc described by the needle.

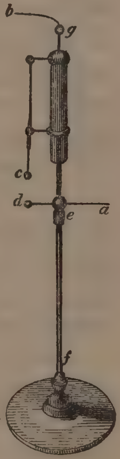
Fig. 4.



Balance Electrometer.—Harris has made a happy application of the common balance and weights to estimate the mutual attraction of oppositely electrified surfaces. The apparatus, figure 4, consists of a brass beam BB′, supported by a conductor CD standing on a wooden frame AA′; *d* is a scale for holding weights, and E its support; *a*, *b*, are gilt cones made of light wood, *a* being suspended by a silver wire from B′, and *b* insulated by the glass support A′*d*′. The instrument is prepared for use by placing *a* and *d* in exact equipoise; the cone *a* is suspended so that its base shall be opposite and parallel to the base of the cone *b*, as may be done by means of three adjusting screws in the frame AA′; and *b* is raised by help of a graduated brass slide *c*, until the bases of the cones are just in contact. The cone *b* is then depressed to any desired distance, which may be varied at will during an experiment, and it is connected with the inner coating of a Leyden jar, the outer coating of which communicates with the frame AA′, and along CDB′ with the cone *a*: these cones may thus be made parts of a charged Leyden jar, and be oppositely excited, as indicated by the signs + and —. The attractive forces exerted between their bases tend to draw down the cone *a* into contact with *b*, discharging the jar; but before it can do so, it has to overcome the weight which may be in the scale *d*. By this ingenious contrivance any number of attractive forces are estimated by a common standard, namely, the number of grains which each is able to raise.

Unit Jar.—This is another contrivance by Harris, and is a most important addition to our stock of electrical apparatus. It is formed of a small inverted Leyden jar, figure 5, supported and insulated by a slender glass rod *ef*, which is covered with lac varnish, and fixed into a wooden frame A. The inner coating of this jar is in metallic contact with a brass ball *d* and a wire *a*, which wire communicates with the prime conductor of an active electrical machine; whereas the brass ball *c* and wire *b* are connected with its outer coating. If the wire *b* be held in the hand, or otherwise communicate with the ground, the electrical machine being in action, the jar is charged in the usual manner, and is discharged by a spark passing between the two brass balls *c* and *d*. The interval may be increased or diminished by causing one of the balls to be moveable by means of a slide or screw. It will be readily conceived that successive sparks through the same interval must be caused by equal quantities of electricity; and experiment shows this to be the case, provided the apparatus is clean and dry, and the charges are taken nearly at the same time, that is, while the air in relation to temperature, pressure, and moisture, may be considered constant. On taking six successive sparks we employ six times as much electricity as for one charge, and three times as much as for two charges, the quantity of electricity being proportional to the number of charges. It is on this account Harris introduced the term unit jar. It is used for charging Leyden jars or batteries with known proportions of electricity.

Fig. 5.



Electric Intensity.—Before concluding this account of electrometers, it will be useful to refer to the kind of information which they supply. From their mode of action, it is plain that they indicate the *degree* of electric excitement, the remoteness from the unexcited state, a condition expressed by the terms *tension* and *intensity*. If two insulated brass disks of equal size be supplied with equal quantities of free electricity, they will affect an electrometer equally, and therefore their intensity or tension is equal; but if one of the disks be larger than the other, the smaller will have the highest tension. In fact, one square inch of the smaller disk will possess more free electricity than the larger, and that is precisely the condition which constitutes differences of intensity. Of any number of electrified substances, that will have the highest intensity which has the most free electric fluid on unity of surface.

LAWS OF ELECTRICAL ACCUMULATION.

1. The quantity of free electricity which an insulated conductor is capable of receiving is independent of its quantity of matter. Thus, two brass spheres of the same size, one solid and the other hollow, will take equal quantities of electricity, and possess equal intensities. The cause of this is referable to the second law.

2. The free electricity of an insulated conductor is always accumulated on its surface, where it forms a layer or stratum enveloping the substance on every side, and therefore possessed of the same figure. The cause of free electricity being disposed upon the surface of conductors is ascribed to the mutual repulsion of its particles, which gives them a tendency to recede as far as possible from each other, and to be arrested at the surface solely by some counteracting force, such as the interposition of an imperfect conductor.

3. The mode in which electricity is distributed over the surface of a conductor is dependent on its figure. On a sphere it forms an uniform stratum of equal thickness all around, that is, each part of the surface has the same quantity of electricity as any other part of equal size. But on an ellipsoid the stratum is thickest at the extremities of the longer axis, and the accumulation at those parts is greater and greater as the length of that axis becomes more and more predominant. In all conductors which are much longer than broad, as in a narrow metallic bar, as also in those which have elongated pointed terminations, the principal accumulation is at the ends and projecting points.*

The unequal accumulation of electricity on conductors is a direct consequence of the law of electric repulsion; and Poisson, assuming the truth of that law, has arrived by calculation at the very same conclusions which Coulomb obtained by experiment. Those who are prepared to follow such very high mathematical inquiries are referred to Poisson's original Essay, to the article on Electricity by Whewell in the Encyclopedia Metropolitana, and to a late work on Electricity by Murphy.

4. The electric fluid accumulated at the surface of conductors

---

* This has been established experimentally by Coulomb.

tends to escape by the repulsion of its particles. Its pressure against the air, or its effort to escape, at any part is considered proportional to the square of the quantity; so that if the electric accumulations at four different parts of an excited conductor are as 1, 2, 3, and 4, the pressure against the air at those parts will be as 1, 4, 9, and 16. Hence electricity passes off with great rapidity from the ends or projecting points of conductors, a result quite conformable to experience. But the equilibrium of an excited conductor is perhaps never entirely restored by the direct diffusion of its excess due to its own repulsion; for the conductor necessarily tends to induce a state opposite to itself in contiguous conductors and in the circumambient air, and then the attraction of oppositely electrified surfaces is called into play.

5. Coulomb proved experimentally, by aid of his torsion electrometer, that the repulsion of two similarly electrified bodies varies inversely as the square of their distances.

6. The attraction of two oppositely electrified bodies varies inversely as the square of the distance between them. Coulomb, who verified this law by experiment, also showed that the attractive force, the distance being constant, varies by the same law as that for repulsion just stated.

Harris has given a beautiful demonstration of these laws by means of his balance electrometer and unit jar (pages 87, 88), the cones *a*, *b*, of figure 4, being connected respectively with the outer and inner coatings of a large Leyden jar. On giving to it a constant charge by means of the unit jar, and varying the distance, the weights raised, or the attractive force, were found to vary inversely as the square of the distance between the cones. On preserving the distance constant, giving a charge capable of raising one grain, and then successively doubling, trebling, and quadrupling the quantity first given to the inner coating, the weights raised were 4, 9, and 16 grains.

7. It may be inferred from the law No. 6, that when, in two oppositely excited bodies, the whole quantity of electricity and the distance vary together and at the same rate, the attractive force will be unchanged. This has been fully proved by Harris. In fact, doubling the electricity on both cones, is to quadruple the attractive force between them; and doubling the distance diminishes the force by four times: the force is thus diminished by one cause as much as it is increased by the other, and therefore continues unchanged.

8. Harris ascertained the nature of the influence exerted by the atmosphere over the striking distance of a charged Leyden jar, that is, the interval through which the electricity will pass, so as to discharge it, by including the balls connected with its outer and inner coating within glass vessels susceptible of exhaustion. He then found that the resistance to the passage of a charge varies as the square of the density of the air. Agreeably to the same law, the striking distance, when the charge is constant, varies inversely as the density of the air: a charge which strikes through one inch of air when the barometer is at 30 inches, will pass through two inches in air so rarefied as to support only 15 inches of mercury, and through four inches when the mercurial column is 7·5 inches. Hence in a perfect vacuum a Leyden jar ought to discharge itself through any interval; and in the higher parts of the atmosphere, where the air is much rarefied, two oppositely-excited clouds will neutralize each other, though separated by very great distances.

It is not apparent from the preceding remarks, whether the striking distance is influenced by change of the density or the elasticity of the confined air, since in rarefying air by the air-pump, the rarefaction increases, and the elasticity decreases at the same rate. Harris has shown, contrary to what one might anticipate, that the influential condition is density, and not elasticity. For on rarefying air by heat so as to preserve its original elasticity, the striking distance was exactly the same as in cold air rarefied to the same degree by the air-pump; and in air first rarefied by the air-pump, and then heated until it had recovered its original elasticity, its volume and density being kept the same, the varied elasticity had no influence on the charge required to pass through a constant distance. From these and similar experiments Harris infers that the remarkable conducting power known to be possessed by hot air is due to its rarity alone.—Though I have not had occasion to repeat these experiments on hot air, I have entire confidence in their accuracy; inasmuch as, not to mention the known skill and exactness of Harris, I find that the striking distance for the same charge is greater in air than in carbonic acid gas, and greater in hydrogen gas than in air, the elasticities being equal.

9. The continuance of an excited charge on an insulated conductor is commonly ascribed to the pressure of the air. An opposite opinion, however, has been maintained. Morgan (Phil. Trans. 1785) published some experiments to prove that a space

entirely free from air, such as a Torricellian vacuum, is a non-conductor of electricity; and Cavallo (Treatise on Electricity) showed that exhaustion may be carried very far within the bell-jar of an air-pump without an electrified body placed under it losing its charge. On repeating these experiments, at the request of Harris, I obtained similar results. These phenomena appear to indicate the existence of an adhesive force between the particles of electricity and the surface of bodies, which causes an obstacle to their escape.

10. Some elegant and most ingenious experiments have been made by Wheatstone to determine the velocity of electricity (Phil. Trans. 1834). His principal conclusions are the following:—

1. The velocity of electricity along a copper wire exceeds that of light through the planetary space.

2. The disturbance of the electric equilibrium in a wire communicating at its extremities with the two coatings of a charged jar, travels with equal velocity from the two ends of the wire, and occurs latest in the middle of the circuit.

3. The light of electricity of high tension has a less duration in passing as a spark than the millionth part of a second.

HISTORICAL NOTICE.

The science of electricity is of modern origin. The knowledge of the ancients was confined to the fact that amber and the *lyncurium* (supposed to be tormalin) acquired the property of attracting light bodies by friction. It was not known that other bodies may be similarly excited until the commencement of the 17th century, when Gilbert of Colchester detected the same property in a variety of other substances, and thereby laid the foundation of the science of electricity. A few additional facts were noticed during the same century by Boyle, Otto de Guericke, and Wall, and in 1709 Hawkesbee published an account of many curious electrical experiments; but no material progress was made until Stephen Grey (Phil. Trans. 1729 to 1733) drew the distinction between conductors and non-conductors of electricity, and illustrated it by new and striking experiments. Soon after, Dufay in France distinguished between the two kinds of electricity; and in 1759 (Phil. Trans. li. 340) Symmer added the important fact that friction developes both kinds of electricity at the same time, an observation which led to the theory of two electric fluids as now understood.

These discoveries, added to the confirmation of Franklin's opinion as to the identity of the cause of lightning and electricity, fixed the attention of scientific men upon the new study, and soon acquired for it a high rank among the sciences.

For further details respecting its origin and early progress the reader may consult the history of electricity by Priestley.

SECTION IV.

GALVANISM.

The science of Galvanism owes its name and origin to the experiments on animal irritability made by Galvani, Professor of Anatomy at Bologna, in the year 1790. In the course of the investigation he discovered the fact, that muscular contractions are excited in the leg of a frog recently killed, when two metals, such as zinc and silver, one of which touches the crural nerve, and the other the muscles to which it is distributed, are brought into contact with one another. Galvani imagined that the phenomena are owing to electricity present in the muscles, and that the metals only serve the purpose of a conductor. He conceived that the animal electricity originates in the brain, is distributed to every part of the system, and resides particularly in the muscles. He was of opinion that the different parts of each muscular fibril are in opposite states of electrical excitement, like the two surfaces of a charged Leyden phial, and that contractions take place whenever the electric equilibrium is restored. This he supposed to be effected during life through the medium of the nerves, and to have been produced in his experiments by the intervention of metallic conductors.

The views of Galvani had several opponents, one of whom, the celebrated Volta, Professor of Natural Philosophy at Pavia, succeeded in pointing out their fallacy. Volta maintained that electric excitement is due solely to the metals, and that the muscular contractions are occasioned by the electricity thus developed passing along the nerves and muscles of the animal. To the experiments instituted by Volta we are indebted for the first voltaic apparatus, which has properly received the name of the *voltaic pile;* and to the same distinguished philosopher belongs the real merit of laying the foundation of the science of Galvanism (Phil. Trans. 1800).

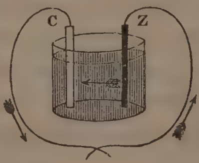
The identity of the agent concerned in the phenomena of galvanism and of the common electrical machine, is now a matter of demonstration. Voltaic and common electricity are due to the same force, excited by different conditions, operating in general in a different manner and under different circumstances. The effects of the latter are caused by a comparatively small quantity of electricity brought into a state of insulation, in which state it exerts a high intensity, as evinced by its remarkable attractive and repulsive energies, and by its power to force a passage through obstructing media. In galvanism the electric agent is more intimately associated with other substances, is developed in large quantity, but never attains a high tension, and produces its peculiar effects while flowing along conductors in a continuous current.

VOLTAIC ARRANGEMENTS OR CIRCLES.

Arrangements for exciting galvanism are divided into simple and compound; the former being voltaic circles in their most elementary form, and the latter a collection of simple circles acting together; it will hence be proper to commence the description of them with the most simple.

Simple Voltaic Circles.—When a plate of zinc and a plate of copper are placed in a vessel of water, and the two metals are made to touch each other, either directly or by the intervention of a metallic wire, galvanism is excited. The action is, indeed, very feeble, and not to be detected by ordinary methods; but if a little sulphuric acid be added to the water, numerous globules of hydrogen gas will be evolved at the surface of the copper. This phenomenon continues uninterruptedly while metallic contact between the plates continues, in which state the circuit is said to be *closed;* but it ceases when the circuit is broken, that is, when metallic contact is interrupted. The hydrogen gas which arises from the copper plate results from water decomposed by the electric current, and its ceasing to appear indicates the moment when the current ceases. In this case the voltaic circle consists of zinc, copper, and interposed dilute acid; and the circle gives rise to a current only when the two metals are in contact. This arrangement is shown in figure 1, where metallic contact is readily made or broken by means of copper wires soldered to the plates. By employing a galvanometer (p. 108), it is found that a current of + electricity continually circulates in the closed circuit from the zinc through the liquid to the copper,

Fig. 1.



and from the copper along the conducting wires to the zinc, as indicated by the arrows in the figure. A current of − electricity, agreeably to the theory of two electric fluids, ought to traverse the apparatus in a direction precisely reversed; but for the sake of simplicity I shall hereafter indicate the course of the + current only.

Two metals are not absolutely essential to the formation of a simple circle. A current is obtained from one metal and two liquids, provided the liquids are such that a stronger chemical action takes place on one side of the metal than on the other. Nay, a plate of metal, with two portions of the same liquid, but of different strengths, forms a simple circle; and even the same liquid, of but one strength, if one side of the metal be more rapidly acted on by it than the other, will produce a current. This may be effected, for example, by having one side rough, the other polished.

An interesting kind of simple voltaic circle is afforded by commercial zinc. This metal, as sold in the shops, contains traces of tin and lead, with rather more than one per cent. of iron, which is mechanically diffused through its substance: on immersion in dilute sulphuric acid, these small particles of iron and the adjacent zinc form numerous voltaic circles, transmitting their currents through the acid which moistens them, and disengaging a large quantity of hydrogen gas. Pure distilled zinc is very slowly acted on by dilute sulphuric acid of sp. gr. ranging from 1·068 to 1·215; but if fused with about 2 per cent. or rather less, of iron filings, it is as readily dissolved as commercial zinc. Sturgeon has remarked that commercial zinc, with its surface amalgamated, which may be done by dipping a zinc plate into nitric acid diluted with two or three parts of water, and then rubbing it with mercury, resists the action of dilute acid fully as well as the purest zinc. This fact, of which Faraday in his late researches has made excellent use, appears due to the mercury bringing the surface of the zinc to a state of perfect uniformity, preventing those differences between one spot and another, which are essential to the production of minute currents; one part has the same tendency to combine with electricity as another, and cannot act as a discharger to it (Faraday).

While the current formed by the contact of two metals gives increased effect to the affinity of one of them for some element of the solution, the ability of the other metal to undergo the same change is proportionally diminished. Thus, when plates of zinc and copper touch each other in dilute acid, the zinc oxidizes more, and the copper less, rapidly than without contact. This principle was beautifully exemplified by the attempt of Davy to preserve the copper sheathing of ships. A sheet of copper immersed in sea-water, or a solution of chloride of sodium, in an open vessel, undergoes rapid corrosion; and a green powder commonly termed submuriate of copper, but which is really an oxy-chloride, is generated: atmospheric oxygen dissolved in sea-water unites both with copper and sodium, the latter yields its chlorine to another portion of copper, and the oxide and chloride of copper unite. But if the copper be in contact with zinc or some metal more electro-positive than itself, the zinc undergoes the same change as the copper did, and the latter is preserved. Davy found that the quantity of zinc required thus to form an efficient voltaic circle with copper was very small. A piece of zinc as large as a pea, or the head of a small round nail, was found fully adequate to preserve 40 or 50 square inches of copper; and this wherever it was placed, whether at the top, bottom, or middle of the sheet of copper, or under whatever form it was used. And when the connection between different pieces of copper was completed by wires, or thin filaments of the 40th or 50th of an inch in diameter, the effect was the same; every side, every surface, every particle of the copper remained bright, whilst the iron or the zinc was slowly corroded. Sheets of copper defended by 1-40th to 1-1000th part of their surface of zinc, malleable and cast iron, were exposed during many weeks to the flow of the tide in Portsmouth harbour, and their weight ascertained before and after the experiment. When the metallic protector was from 1-40th to 1-150th, there was no corrosion nor decay of the copper; with smaller quantities, such as 1-200th to 1-460th, the copper underwent a loss of weight which was greater in proportion as the protector was smaller; and as a proof of the universality of the principle, it was found that even 1-1000th part of cast iron saved a certain proportion of the copper (Phil. Trans. 1824).

Unhappily for the application of this principle in practice, it is found that unless a certain degree of corrosion takes place in the copper, its surface becomes foul from the adhesion of sea-weeds and shell-fish. The oxy-chloride of copper, formed when the sheathing is unprotected, is probably injurious to these plants and animals, and thus preserves the copper free from foreign bodies.

Simple voltaic circles may be formed of very various materials:

but the combinations usually employed consist either of two perfect and one imperfect conductor of electricity, or of one perfect and two imperfect conductors. The substances included under the title of perfect conductors are metals and charcoal, and the imperfect conductors are water and aqueous solutions. It is essential to the operation of the first kind of circle, that the imperfect conductor act chemically on one of the metals; and in case of its attacking both, the action must be greater on one metal than on the other. It is also found generally, if not universally, that the metal most oxidized is positive with respect to the other, or bears to it the same relation as zinc to copper in figure 1. Davy, in his Bakerian lecture for 1826 (Phil. Trans.), to which the reader is referred, has given lists of different arrangements of both the kinds just mentioned.

Faraday has shown that the presence of water is not essential. A battery may be composed of other liquid compounds, such as a fused metallic chloride, iodide, or fluoride, provided it is decomposable by galvanism, and acts chemically on one metal of the circle more powerfully than on the other.

Metallic bodies are not essential to the production of galvanic phenomena. Combinations have been made with layers of charcoal and plumbago, of slices of muscle and brain, and beet-root and wood; but the force of these circles, though accumulated by the union of numerous pairs, is extremely feeble, and they are very rarely employed in practice.

Of the simple voltaic circles described by Davy, the only one used for ordinary purposes is that composed of a pair of zinc and copper plates excited by an acid solution arranged as in figure 1. The form and size of the apparatus are exceedingly various. Instead of actually immersing the plates in the solution, a piece of moistened cloth may be placed between them. Sometimes the copper plate is made into a cup for containing the liquid, and the zinc is fixed between its two sides, as shown by the accompanying transverse vertical section, figure 2; care being taken to avoid actual contact between the plates, by interposing pieces of wood, cork, or other imperfect conductor of electricity. Another contrivance, which is much more convenient, because the zinc may be removed at will and have its surface cleaned, is that represented by the annexed woodcut (fig. 3). C is a cup made with two cylinders of sheet copper, of unequal size,

Fig. 2.

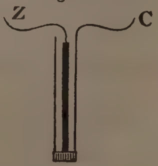
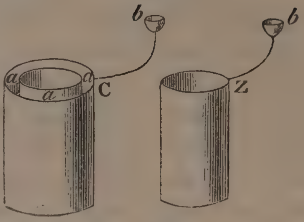


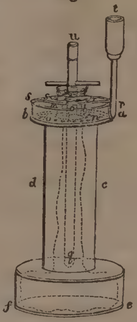
Fig. 3.



placed one within the other, and soldered together at bottom, so as to leave an intermediate space *a a a*, for containing the zinc cylinder z and the acid solution. The small copper cups *b b* are useful appendages; for by filling them with mercury, and inserting the ends of a wire, the voltaic circuit may be closed or broken with ease and expedition. This apparatus is very serviceable in experiments on electro-magnetism.

Another kind of circle may be formed by coiling a sheet of zinc and copper round each other, so that each surface of the zinc may be opposed to one of copper, and separated from it by a small interval. The London Institution possesses a very large apparatus of this sort, made under the direction of Pepys, each plate of which is 60 feet long and two wide. The plates are prevented from coming into actual contact by interposed ropes of horsehair; and the coil, when used, is lifted by ropes and pulleys, and let down into a tube containing dilute acid. The contrivance of opposing one large connected surface of zinc to a similar surface of copper originated with Hare of Philadelphia, who, from its surprising power of igniting metals, gave it the name of *calorimotor.*

Fig. 4.



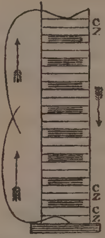
An excellent arrangement has been described by Daniell, of which fig. 4 represents a modification more simple and perhaps equally effective. It consists of a cylinder of copper, *a b c d e f*, 3 inches wide from *a* to *b*, $1\frac{1}{2}$ inches from *c* to *d*, and four inches from *e* to *f*, the corresponding heights being half an inch, 5 inches, and 2 inches; *l m n o*, is a collar of copper, which by the arms *r r*, *s s*, rests on the top of the cylinder, and to which a membranous tube formed of the gullet of an ox is tied, the membrane being longer than the copper cylinder, so as to be baggy below and nearly fill the space *e f*; *u p q*, is a rod of amalgamated zinc resting on the collar *l m n o*, by means of a piece of wood *r s*, which perforates it; *u*, *t*, are cups to hold mercury for making contact. Between the membrane and copper cylinder is poured a saturated solution of blue vitriol, and within the membrane dilute sulphuric acid of about sp. gr. 1·136, which is made with 1 measure of strong acid and 8 of water. The exciting acid is thus in contact with the zinc, but not with the copper. When this circle is in action, the electric current passes from the zinc through the acid, membrane, and solution of blue vitriol to the copper. The arrangement is founded on two important principles, established by Daniell :—

1. However active a circle, as made heretofore, may be when first excited, its energy is known rapidly to diminish, and in a few minutes to fall much below its original power. Daniell has traced the cause to reduction of oxide of zinc by nascent hydrogen at the surface of the copper plate, whereby this metal becomes coated with zinc, and is thus more or less converted at its surface into a zinc plate; and as two zinc plates under like conditions do not produce a current, of course the action declines. In the new circle this defect is avoided by the membranous septum which protects the copper plate from contact with the solution of zinc: the nascent hydrogen reduces oxide of copper, and a film of bright copper is deposited on the copper plate, thus constantly presenting a clean good conducting surface; while the hydrogen itself, not escaping as gas, no longer opposes an obstacle, as it does when allowed to assume the gaseous form, to the passage of electricity, from the solution to the copper plate. To supply the loss of oxide of copper, a copper disc, *a*, *v*, *x*, *b*, studded with holes like a cullender, is supplied, on which rest crystals of blue vitriol, whereby the solution is kept saturated, and its conducting power preserved. When the acid within the membrane is exhausted, the membrane itself is removed, and fresh acid supplied; but to prevent the necessity of frequent renewal, the lower part of the membrane is made to act as a reservoir of acid.

2. The zinc of a pair of plates may be much reduced in size without any loss of power: strong chemical action on a small surface of zinc, a good conducting solution, and a bright large surface of copper, are conditions by which a powerful action is ensured. This is indicated by Davy's protectors for copper sheathing (page 96); but it was not previously known that the principle was applicable to the construction of voltaic apparatus. The great merit of this circle is its *constancy:* by keeping up the supply of blue vitriol and acid, its energy will continue invariable for hours, or for an indefinite period. A similar apparatus has been described by Mullins (Phil. Mag. & An. ix. 122).

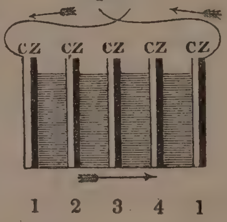
Compound voltaic circles.—This expression is applied to voltaic arrangements which consist of a series of simple circles. The first combinations of the kind were described by Volta, and are now well known under the names of *voltaic pile* and *crown of cups.* The voltaic pile is made by placing pairs of zinc and copper, or zinc and silver plates, one above the other, as in figure 5, each pair being separated from those adjoining by pieces of cloth, rather smaller than the plates, and moistened with a saturated solution of salt. The relative position of the metals in each pair must be the same in the whole series; that is, if the zinc be placed below the copper in the first pair, the same order should be observed in all the others. Without such precaution the apparatus would give rise to opposite currents, which would neutralize each other more or less according to their relative forces. The pile, which may consist of any convenient number of combinations, should be contained in a frame formed of glass pillars, fixed into a piece of thick dry wood, by which it is both supported and insulated. Any number of these piles may be made to act in concert by establishing metallic communication between the + extremity of each pile and the — extremity of the pile immediately following.

Fig. 5.



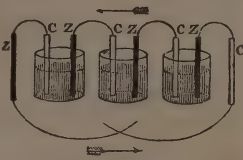
The voltaic pile is now rarely employed, because we possess other modes of forming galvanic combinations which are far more powerful and convenient. The galvanic battery proposed by Cruickshank consists of a trough of baked wood, about 30 inches long, in which are placed at equal distances 50 pairs of zinc and copper plates previously soldered together, and so arranged that the same metal shall always be on the same side. Each pair is fixed in a groove cut in the sides and bottom of the box, the points of junction being made water-tight by cement. The apparatus thus constructed is always ready for use, and is brought into action by filling the cells left between the pairs of plates with some convenient solution, which serves the same purpose as the moistened cloth in the pile of Volta. By means of the accompanying woodcut the mode in which the plates are arranged will easily be understood.

Fig. 6.



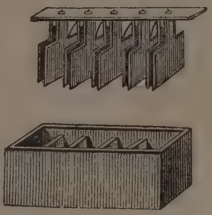
Other modes of combination are now in use, which facilitate the employment of the voltaic apparatus and increase its energy. Most of these may be regarded as modifications of the crown of cups. In this apparatus the exciting solution is contained in separate cups or glasses, disposed circularly or in a line; each glass contains a pair of plates; and each zinc plate is attached to the copper of the next pair by a metallic wire, as represented in figure 7. Instead of glasses, it is more convenient in practice to employ a trough of baked wood or glazed earthenware, divided into separate cells by partitions of the same material; and in order that the plates may be immersed into and taken out of the liquid conveniently and at the same moment, they are all attached to a bar of dry wood, the necessary connection between the zinc of one cell and the copper of the adjoining one being accomplished, as in figure 8, by a slip or wire of copper.

Fig. 7.



A material improvement in the foregoing apparatus was suggested by Wollaston (Children's Essay in Phil. Trans. 1815), who recommended that each cell should contain one zinc and two copper plates, so that both surfaces of the former metal might be opposed to one of the latter. The plates communicate with each other, and the zinc between them with the copper of the adjoining cell. An increase of one half the power is said to be obtained by this method.

Fig. 8.



The size and number of the plates may be varied at pleasure. It is now recognized, however, that increasing the number of plates beyond a very moderate limit gives for most purposes no proportionate increase of power; so that a battery of 50 or 100 pair of plates, thrown into vigorous action, will be just as effective as one of far greater extent.

A very effective battery, which, I apprehend, from its constancy of action, convenience, cheapness, and power, will supersede all others, is made with Daniell's simple circles (page 98). Twenty of these, arranged on a wooden tray in two rows, has an energy sufficient for the performance of most experiments of demonstration or research.

It must be remembered that in a compound circle, the extreme plates at either end, not being in contact with the exciting fluid, are in reality superfluous, and serve only as conductors. Hence the current, instead of flowing from the zinc to the copper, seems to flow from the copper to the zinc. But if we abstract the extreme plates, which serve only as conductors, it is then seen that the direction of the current corresponds to that of the simple circle (see fig. 5).

During the action of a simple circle, as of zinc and copper, excited by dilute sulphuric acid, all the hydrogen developed in the voltaic process is evolved at the surface of the copper. This fact is not apparent when common zinc plates are used, owing to the numerous currents which form on the surface of the zinc (page 95); but when a plate of amalgamated zinc and another of platinum are introduced into dilute sulphuric acid of sp. gr. 1·068, no gas whatever appears until contact between the plates is made, and then hydrogen gas rises solely from the platinum, while zinc is tranquilly dissolved. On weighing the amalgamated plate before and after the action has continued for half an hour or an hour, and collecting the hydrogen gas evolved during that interval, the weight of the hydrogen set free and of zinc dissolved will be as 1 to 32·3, being the ratio of their chemical equivalents. Faraday, who has proved this, has also shown that in a compound voltaic circle, say of 10 amalgamated zinc plates and 10 of platinum, each of the former during a given period of action loses exactly the same weight, and from each of the latter an equivalent quantity of hydrogen gas is evolved. This separation of one ingredient of the exciting solution at one plate, while the element previously combined with it unites with the other plate, seems essential to voltaic action. It is in some way connected with the passage of the current across the exciting liquid. Oxygen in a free state may by oxidizing zinc cause electric excitement; but the voltaic current is not established unless the oxygen formed part of a previous liquid compound in contact or communication with both the plates.

Among the different kinds of voltaic apparatus is usually placed the electric column of De Luc, which is formed of successive pairs of silver and zinc, or silver and Dutch-metal leaf, separated by pieces of paper, arranged as in a voltaic pile. It is remarkable for its power of exhibiting attractions and repulsions like common electricity, but cannot produce chemical decomposition or any of the effects most characteristic of a voltaic current, and is rather an electrical than a voltaic instrument. It is quoted as a proof of electric developement by contact, since it will continue in action for years without being cleaned or taken to pieces. True it is that the more oxidable metal of the column is slowly corroded, and that no electricity is excited when the paper is quite or nearly free from hygrometric moisture, the presence of which is necessary to the oxidation of the zinc and copper; but at the same time the quantity of electricity excited seems so disproportioned to the corrosion, that the one can scarcely be assigned as the cause of the other.

LAWS OF THE ACTION OF VOLTAIC CIRCLES.

Electricians distinguish between *quantity* and *intensity* in galvanism, as in ordinary electricity (page 88); and by most persons, as also in this work, the same meaning is attached to them. The electric intensity of a voltaic circle is most correctly estimated by the divergence which in the broken circuit it causes in a gold leaf or other electrometer; and as the intensity is never considerable, it is often necessary to employ a condenser. The charges accumulated on the extreme plates of a voltaic circle cannot acquire a high tension, because the liquid which separates them is a good conductor for all charges except such as are of very feeble intensity. Accordingly, a simple circle has necessarily a very feeble tension. The circle which gives the highest tension is one which excites electricity sufficient for duly charging the apparatus, while it opposes an obstacle to spontaneous discharge. A battery of numerous small plates excited by water, or a weak saline or acid solution, fulfils these conditions.

The quantity of electricity circulating in a voltaic battery is exactly the same in all its parts. It is found to be exactly proportional to the magnetic and chemical effects which it is capable of producing; and hence the quantity of electricity moving through any closed circuit is readily estimated either by the deflection which it causes on a magnetic needle, or by its power of chemical decomposition. When quantity of electricity is alone desired, a single pair of plates is just as useful as a compound circle.

The following numerical results were obtained by Ritchie by means of a magnetic galvanometer:—

1. The power of a single pair of plates in deflecting the magnetic needle is directly proportional to the surface of the plates which is covered with dilute acid.

2. A plate of zinc introduced into a rectangular cup of copper,

as in figure 2, page 97, deflects the needle twice as much as when one side of the zinc and the adjacent surface of copper are protected by a coating of cement from the action of the acid solution.

3. The deflection produced by a pair of plates, in an acid solution of uniform strength, varies inversely as the square root of the distance between them,—a law previously established by Cumming.

4. The same law, as previously deduced by Cumming and Barlow, applies to variations in the length of the wire by which the zinc and copper plates are connected. If, all other circumstances being uniform, the conducting wire varies from 4 feet to 1 foot in length, the deflecting power will vary in the ratio of 1 to 2. Ritchie has stated that with short metallic wires the deflection varies inversely as the square root of the length of the whole circuit, that is, of the solid and liquid conductors taken together.

Ritchie has also shown, agreeably to general observation, that the deflecting power of a compound circle is not increased by increasing the number of its plates. This is another proof that the direct influence of a number of plates is to increase the intensity and not the quantity of electricity; for the prevailing opinion that the magnetic needle takes no cognizance of intensity is fully borne out by the experiments of Faraday.

Though the quantity of a compound decomposed by a battery is proportional to the actual quantity of electricity which passes, yet, as a compound exposed to voltaic action is almost always an imperfect conductor, the quantity of electricity capable of passing through it varies with its intensity. Hence chemical decomposition depends on quantity and intensity together, and affords a criterion of the increased tension of a compound circle due to an increase in the number of its plates.

EFFECTS OF GALVANISM.

The effects producible by voltaic combinations are conveniently divisible into the electrical, magnetic, and chemical phenomena.

I. *Electrical Effects.*—These are so called, as being analogous to the effects of ordinary electricity. An active broken circuit produces the phenomena of electric repulsion, as already stated (page 101). A Leyden phial may also be charged by contact of its inner coating with one wire of the circle, while the outer communicates either with the other wire or with the ground: a full charge, though of feeble intensity, is almost instantly given. On approximating the wires of an active circle, a brilliant spark passes between them just before contact, as well as in the act of breaking contact. When the electric current is made to pass through the body of an animal, as on holding the conducting wires in the hands, previously moistened to facilitate conduction, a distinct shock is felt, which is powerful when a battery of high tension is employed. On sending the current through fine metallic wires or slender pieces of plumbago or compact charcoal, these conductors become intensely heated, the wires even of the most refractory metals are fused, and a vivid white light appears at the charcoal points equal, if not superior, in splendour to that of phosphorus burning in oxygen gas; a phenomenon in no wise referable to combustion, as it takes place in a vacuum or under water. If the electric current pass through thin metallic leaves, the metals burn with vivid scintillations:—gold leaf emits a white light tinged with blue, silver a beautiful emerald green light, copper a blueish white light with red sparks, lead a rich purple, and zinc a brilliant white light fringed with red. In burning leaves, fusing wire, and igniting charcoal, a large quantity of electricity is the only requisite: the large battery of Children, though capable of fusing several feet of platinum wire, had an electric tension so feeble, that it did not affect the gold leaves of the electrometer, gave a shock scarcely perceptible even when the hands were moist, communicated no sensible charge to a Leyden jar, and could not produce chemical decomposition. If the quantity and intensity of the current are both great, an arc of light appears between the charcoal points after contact, even through an interval of an inch or more.

The electrical effects of galvanism are so similar to those of the electrical machine, that it is impossible to witness and compare both series of phenomena without referring them to the same agent. The question of identity early occupied the attention of Wollaston, who made some very beautiful and conclusive experiments to prove that not only are the electrical effects of the machine producible by galvanism, but that the chemical effects of galvanism may be characteristically produced by a current from the electrical machine (Phil. Trans. 1801). The subject has been examined anew by Faraday, who has subjected the effects of electricity and galvanism to a minute and critical comparison: he has obtained ample proof of the decomposing power of an electric current from an electrical machine, both by repeating the experiments of Wollaston and devising new ones of his own. He has also completed the chain of evidence by deflecting a magnetic needle with an electric current from the machine; an observation, indeed, which had been previously made by Colladon. These researches have led to a remarkable contrast between the quantity of electricity concerned in the production of voltaic and ordinary electrical phenomena. Faraday states that the quantity of electric fluid employed in decomposing a single grain of water is equal to that of a very powerful flash of lightning; and this statement, surprising as it is, is supported by such strong evidence, that it is difficult to withhold assent to the assertion.

II. *Magnetic Effects of Galvanism.*—The power of lightning in destroying and reversing the poles of a magnet, and in communicating magnetic properties to pieces of iron which did not previously possess them, was noticed at an early period of the science of electricity, and led to the supposition that similar effects may be produced by the common electrical and voltaic apparatus. Attempts were accordingly made to communicate the magnetic virtue by means of electricity and galvanism; but no results of importance were obtained till the winter of 1819, when Oersted of Copenhagen made his famous discovery, which forms the basis of a new branch of science. (An. Phil. xvi. 273.)

The fact observed by Oersted was, that the metallic wire of a closed voltaic circle,—and the same is true of charcoal, saline fluids, and any conducting medium which forms part of a closed circle,—causes a magnetic needle placed near it to deviate from its natural position, and assume a new one, the direction of which depends upon the relative position of the needle and the wire. On placing the wire above the magnet and parallel to it, the pole next the negative end of the battery always moves westward; and when the wire is placed under the needle, the same pole goes towards the east. If the wire is on the same horizontal plane with the needle, no declination whatever takes place; but the magnet shows a disposition to move in a vertical direction, the pole next the negative side of the battery being depressed when the wire is to the west of it, and elevated when it is placed on the east side.

When the influence of the earth's magnetism on the needle which impedes its free motion, is counteracted by another magnet placed near it, the needle places itself directly across the connecting wire; so that the real tendency of a magnet is to stand at right angles to an electric current.

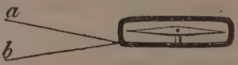
The communicating wire is also capable of attracting and repelling the poles of a magnet. When the connecting wire is held vertically near a horizontally suspended magnet, on the west side of it, and approached to the north pole, attraction ensues, till they come very close, when repulsion follows. When the wire is approached to the south pole, similar effects ensue, in an inverted order. If the wire be held on the east side, the effects are reversed; the current in both cases being supposed to flow upwards through the wire.

The discovery of Oersted was no sooner announced, than the experiments were repeated and varied by philosophers in all parts of Europe, and, as was to be expected, new facts were speedily brought to light. Among the most successful of those who early distinguished themselves were Ampère, Biot, and Arago, of Paris, and Davy and Faraday in this country. A host of other able men have since added their contributions; and their joint labours have established an altogether new science, *Electro-Dynamics*, which has already become one of the most important branches of physical knowledge, and still offers a rich harvest of discovery to its cultivators. Those who wish to enter deeply into the study of this subject should consult the *Recueil d'Observations Electro-Dynamiques* by Ampère, Cumming's Manual of Electro-Dynamics, Murphy's Treatise on Electricity, and the second edition of Barlow's Essay on Magnetic Attractions. A less mathematical, and therefore more generally intelligible, treatise has been drawn up with great ability by Roget, and published as part of the Library of Useful Knowledge; and a Popular Sketch of Electro-Magnetism has been given by Watkins of Charing-cross. To these works I refer as supplying that detail of the facts and theories of electro-dynamics, which, as belonging more to the province of physics than chemistry, is unsuited to the design of this volume.

The phenomena of electro-dynamics are solely produced by electricity in motion. The passage of electricity through solid or liquid conductors is essential; in fact, a magnetic needle is a *galvanoscope*, by which means the existence and direction of an electric current may be detected. In this way, Ampère demonstrated the fact, that electricity passes uninterruptedly through the battery when the circuit is closed, and not at all in the broken circuit.

But a magnetic needle will not only indicate the existence and direction of an electric current: it may even serve, by the degree of deflection, as an exact measure of its force. When used for this purpose, under the name of *galvanometer*, some peculiar arrangements are required in order to ensure the requisite delicacy and precision. Experiment proves that a magnet is equally affected by every point of a conductor along which an electric current is passing; so that a wire transmitting the same current will act with more or less energy, according as the number of its parts contiguous to the needle is made to vary. On this principle is constructed the *Galvanometer* or *Multiplier* of Schweigger. A copper wire is bent into a rectangular form consisting of several coils, and in the centre of the rectangle is placed a delicately suspended needle, as shown in figure 9. Each coil adds its influence to that of the others; and as the current, in its progress along the wire, passes repeatedly above and below the needle in opposite directions, their joint action is the same. In order to prevent the electricity from passing laterally from one coil to another in contact with it, the wire should be covered with silk. The ends of the wire, *a* and *b*, are left free for the purpose of communication with the opposite ends of the voltaic circle. The needle ought to be rendered *astatic*, that is the influence of the earth's magnetism ought to be destroyed by placing another magnet above the rectangle, having its north pole adjacent to the south pole of the first. The instrument is thus rendered extremely delicate.

Fig. 9.

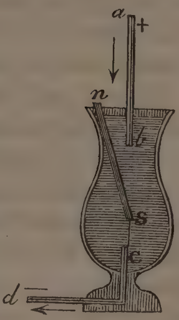


The mutual influence of a magnetic pole and a conducting wire changes with distance between them; and experiment leads to the conclusion that the attraction of a magnetic pole on a *single* point of a conductor varies as the square of the distance; the same well known law which regulates the distribution of heat and light, as well as electricity.

On examination, all the phenomena described by Oersted are found to be referable to a force acting tangentially on the poles of a magnet, and in a plane perpendicular to the direction of the current.

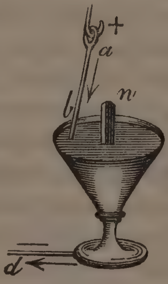
The same principle accounts for the rotation of a magnetic pole round a current, discovered by Faraday. Into the centre of the bottom of a cup, as in the vertical section, figure 10, a copper wire c *d* was inserted, a cylindrical magnet *n* s was attached by a thread to the copper wire c, and the cup was nearly filled with mercury, so that pole *n* only of the magnet projected. A conductor *a b* was then fixed in the mercury perpendicularly over the wire c. On connecting the conducting wires with the opposite ends of a battery, a current was transmitted from one wire through the mercury to the other. If the + current descend, the north pole of the magnet, if uppermost, will rotate round the wire *a b*, passing from east through the south to west like the movements in the hands of a watch; and if the current ascend, the line of rotation will be reversed. Under similar circumstances the south pole would in each case rotate in the opposite direction.

Fig. 10.



If a magnetic pole rotate round a conductor, a conductor will be equally disposed to rotate round a magnetic pole, just as a magnet moves towards iron or iron towards a magnet, according as one or other is free to move. Accordingly, on fixing a magnet vertically in the middle of a cup of mercury, fig. 11, and transmitting a current by the movable conductor *a b* through the mercury, and along a second conductor *d*, fixed as before in the bottom of the cup, Faraday found that the free extremity *b* of the wire moved round the pole of the magnet in a direction similar to the last.

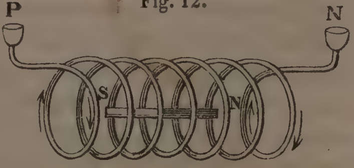
Fig. 11.



It is obvious that the direction of rotation imparted by a fixed current to the movable pole, will be identical with that which the same pole tends to impart to the same current.

A current of voltaic electricity not only determines the position of a magnet, but renders steel permanently magnetic. This was observed nearly at the same time by Arago and Davy, who found that when needles are placed at right angles to the conducting wire, permanent magnetism is communicated; and Davy also succeeded in producing this effect even with a shock of electricity from a Leyden phial. Arago, at the suggestion of Ampère, made a voltaic conductor into the form of a helix, into the axis of which he placed a needle, as in figure 12. As in

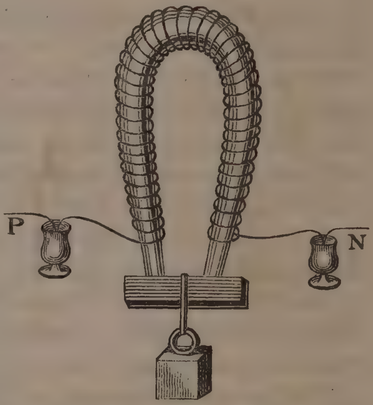
Fig. 12.



this arrangement the current nearly in every part of its course is at right angles to the needle, and as each coil adds its effect to that of the others, the united action of the helix is extremely powerful. The needle was thus fully magnetized in an instant.

Though soft iron does not retain magnetism, its magnetic properties while under the influence of an electric current are very surprising. A piece of soft iron about a foot long and an inch in diameter is bent into the form of a horse-shoe, a copper wire is twisted round the bar at right angles to its axis, and an armature of soft iron, to which a weight may be attached, is fitted to its extremities, as in figure 13. On connecting the ends of the wire with a simple voltaic circle, even of small size, the soft iron instantly becomes a powerful magnet, and will support considerable weights. Increasing the number of coils gives a great increase of power; but as the length of wire required for that purpose diminishes the influence of the current (page 104), the following arrangement has been successfully adopted. The total length of copper wire intended to be used is cut into several portions, each of which, covered with silk or cotton thread to prevent lateral communication, is coiled separately on the iron. The ends of all the wires are then collected into two separate parcels, and are made to communicate with the same voltaic battery, taking care that the + current shall pass along each wire in the same direction. The current is thus divided into a number of branches, and has only a short passage from one end of the battery to the other, though it gives energy to a multitude of coils. A combination of this kind, connected with a battery of five feet square, supported 2063 pounds, or nearly a ton weight.

Fig. 13.



In witnessing the influence of voltaic conductors over the directive property of magnets, and in inducing magnetism, it is difficult to divest one's self of the conviction that these conductors, while transmitting a current, are themselves magnetic. This belief was early entertained by those who repeated the experiments of Oersted, and experimental evidence of its truth was speedily adduced.

Arago and Davy found that a copper wire connecting the end of a voltaic combination attracted iron filings, but that they instantly fell off as soon as the circuit was broken; and a conductor, when its movements were not impeded by friction or gravity, was proved by Ampère to be obedient, like an ordinary magnet, to the magnetic agency of the earth.

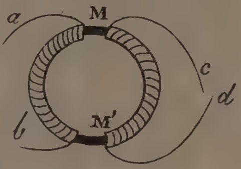
Since, therefore, the conductors just described may be regarded as magnets, such magnetized conductors ought mutually to repel or attract each other, when poles of the same or a different nature are adjacent; and as the action of a whole spiral or rectangle is merely the accumulated effect of its individual parts, it is fair to presume that each small portion of a conductor has its opposite sides in a state of opposite polarity, and that two such contiguous portions should attract or repel each other on the same principle as the spirals of which they constitute a part. Nay, even different parts of the same conductor ought to be mutually attractive or repulsive. These inferences from the facts already detailed were fully demonstrated by Ampère soon after the discovery of Oersted. He proved that two voltaic conductors, or two portions of the same conductor, attract each other when the currents have the same direction, and are mutually repulsive when they are traversed by opposite currents; which is exactly what would be anticipated from the magnetic influence of conductors.

These are a few examples of the numerous facts experimentally proved by Ampère concerning the action of voltaic conductors on each other. It is to this branch of the subject the term of *Electro-Dynamics*, or the science of electricity in motion, is sometimes restricted, while the mutual action of conductors and magnets is called *Electro-Magnetism;* but these two branches are so entirely parts of the same science, that I have included both under Ampère's term of Electro-Dynamics. Any one who has studied the few preceding pages with moderate care, cannot fail to trace a close analogy between a helix traversed by an electric current and a magnet. The former is effected by other voltaic conductors, by the poles of a magnet, and by the magnetism of the earth, in the same manner as the latter. It was this similarity, or rather identity, of action which led Ampère to his theory of magnetism. He supposes that the polarity of every magnet is solely owing to the circulation, within its substance and at its surface, of electric currents, which continually pass around all its particles in planes perpendicular to its axis. On placing a magnet in its natural position of north and south, the direction of its currents is as follows; they descend on the east side, passing under the magnet from east to west, and ascending on the side next the west. In like manner are currents supposed to circulate within the earth, especially near its surface, passing from east to west in planes parallel to the magnetic equator. These terrestrial currents cause all bodies, which are freely suspended, and are possessed of electric currents, to place themselves in such a position that the current on their under side should flow in parallelism, and in the same direction, with that in the earth immediately beneath. That the existence of such currents will account for the directive property of the earth, follows from the mutual action of conductors; and Barlow, to render the analogy still more complete, constructed a hollow sphere of wood in which electric currents were made to circulate in the same direction as they are thought to do in the earth; and by placing an astatic needle on different parts of its surface, he found that all the phenomena of terrestrial magnetism might be imitated. Observation has even supplied a cause for the existence of currents in the earth, moving in the direction which theory requires. The diurnal rotation of our planet on its axis exposes its surface to be heated in a direction passing from east to west; and the discoveries which have been made in thermo-electricity (page 81) sufficiently prove the probability of electric currents being established in the conducting matter of the earth by the successive heating of its parts. In short, the theory of Ampère connects the facts of electro-dynamics with the phenomena of terrestrial magnetism, and affords a splendid instance of the application of mathematical analysis to physical research.

Volta-electric Induction.—The developement of electricity by the vicinity of an excited body, already described under the name of induced electricity (page 82), led Faraday to inquire whether electricity in motion, as well as that of tension and at rest, may not be excited by induction. Though baffled in his early attempts, he at last succeeded in laying open a new branch of electro-dynamics, which vies in interest and importance with the fundamental discovery of Oersted (Phil. Trans. 1831). A copper wire 203 feet long was passed in form of a helix round a large block of wood, and an equal length of a similar wire was wound on the same block and in the same direction, so that the coils of each helix should be interposed, but without contact, between the coils of the other. The ends of one of the helices were connected with a galvanometer, and the other with a strong galvanic battery, with the view of ascertaining whether the passage of an electric current through one helix would induce a current in the adjoining helix. It was found that the galvanometer needle indicated a current at the moment both of completing and breaking the circuit, but that in the interval no deflection took place; and similarly the induced currents readily magnetized a sewing needle, while the electric current along the inducing helix was in the act of beginning or ceasing to flow, but at no other period. In the former case the direction of the induced current is opposite to that of the inducing current, and in the latter case it is the same. This phenomenon is distinguished by Faraday under the name of *volta-electric induction.*

The inducing power of a magnet greatly exceeds that of an electric current. A ring of soft iron was covered to nearly half its extent by several helices, the ends of which were brought together so as to constitute a compound helix terminating in the conductors *a b*, figure 14; and on the other half of the ring were arranged similar helices which communicated by *c d* with a galvanometer. The two sets of helices were thus separated from each other by portions of the ring M M′, and were protected by cloth from direct contact with the ring itself. At the moment the wires *a b* touched the ends of a voltaic combination, the galvanometer was strongly affected: the needle then returned to its former position and remained there until the voltaic circuit was broken, when the needle was again deflected as strongly as before, but in the opposite direction. The action was still greater when both compound helices were on the same part of the ring, the induction being increased apparently by the closer contiguity of the helices. Other arrangements have been devised by Faraday, for producing similar results; and to the action in all these cases he has given the name of Magneto-electric induction.

Fig. 14.



The phenomena arising from magneto-electric and volta-electric induction are manifestly owing to the same condition of the induced wire: the action on the needle, though different in force, is identical in kind. It is equally clear that the agent brought into operation in the induced wire is an electric current, or, to dismiss the language of theory, that the induced wire is in the same electric state as the conducting wire in a closed voltaic circle. Its power in magnetizing steel and deflecting a magnet is sufficient evidence of this; but Faraday, by magneto-electric induction, succeeded in throwing a frog's leg into spasms by connecting it with the induced wire, and by arming the ends of that wire with points of charcoal, and separating them at the instant the galvanic circuit of the inducing wire was broken or restored, sparks of electricity were obtained. The mode in which soft iron contributes to the effect is likewise obvious. An electric current circulating round a bar of soft iron has been shown to convert it into a temporary magnet possessed of surprising power (page 110); and it is doubtless to this magnet, called into temporary existence by the electric current, most of the induced electricity is to be ascribed. Faraday reduced this to certainty by surrounding a cylinder of soft iron with one helix connected with the galvanometer, and converting the soft iron into a temporary magnet, not by a voltaic battery, but by placing at each end of the cylinder the opposite pole of a magnet. During the act of applying the magnetic poles to the iron, the galvanometer needle was deflected; and the deflection was reproduced, but in the opposite direction, when the magnetism of the iron was ceasing by the removal of the magnet. Similarly, when a helix was wound on a hollow cylinder of pasteboard, and a real magnet was introduced, the galvanometer was deflected: the needle then remained quiescent so long as the magnet was left in the cylinder; but in the act of its removal, the needle was again deflected, though, as usual, in the opposite direction.

These singular phenomena, which establish such new and intimate relations between voltaic and magnetic action, and supply additional evidence in favour of Ampère's beautiful theory of magnetism, have led to an experiment by which, at first view, an electric spark appeared to be derived from the magnet itself. After Faraday had announced his experiment, above mentioned, of obtaining a spark from the induced wire, other attempts were made to effect the same object with a magnet, without the aid of galvanism. The first person who succeeded in this country was Forbes, who operated with a powerful loadstone (Phil. Trans. Ed. 1832). A helix of copper wire was formed round the middle of a cylinder of soft iron, which was of such length that its extremities reached from one pole of the loadstone to the other. On applying and withdrawing the soft iron cylinder to and from the poles of the loadstone, magnetism was alternately created and destroyed within it.

At these periods of transition, electric currents were induced in the helix surrounding the soft iron; and when, at these instants, metallic contact between the conducting wires of the helix was broken, an electric spark was visible. Forbes succeeded best by connecting one wire with a cup of mercury, and removing the other wire from contact with its surface at the instant when an assistant withdrew the armature of soft-iron from the loadstone. In this experiment, therefore, the electricity was obtained from the helix, and was induced in it by the soft iron while in the act of acquiring or losing magnetism. The same experiment was performed by Faraday with a loadstone belonging to Daniell; and shortly before the experiment of Forbes, Nobili and Antinori succeeded with an ordinary steel magnet. Pixii in Paris afterwards performed this experiment with great effect by causing a strong horse-shoe magnet to revolve upon an axis, its poles passing in rapid succession in front of a soft iron armature of the same form; and a still better arrangement is to cause the armature to revolve in front of the poles of a powerful magnet, as in the instrument fitted up by Saxton, and exhibited at the Adelaide-rooms, London. It produces brilliant sparks, renders platinum wire red hot, and gives a strong shock. It explodes gunpowder, and also a mixture of oxygen and hydrogen gases, and decomposes water rapidly.

Intimately associated with magneto-electric induction, if not referable to the very same origin, is the induction of electric currents by movement. On introducing a magnet into a hollow helix of copper wire, or other solid conductor, as also on withdrawing the magnet after its introduction, an electric current was momentarily induced in the wire; and if, the magnet being stationary, the helix were moved in its vicinity, an electric current is likewise induced. The direction of the movement is not immaterial: it is essential that the plane in which the conductor moves should form an angle with the axis of the magnet; and the most powerful currents were induced, when the plane of motion was at right angles to that axis, and hence parallel to the electric currents which Ampère supposes to exist in the magnet. With regard to the direction of an induced current, Faraday's researches establish this law, deduced by Ritchie: if a wire conducting voltaic electricity produce on magnets or conductors certain motions, whether repulsive, attractive, or rotatory, and if the battery be removed, the ends of the wires brought into metallic contact, and the same motions be produced by mechanical means, the conductor will have the same electric state induced in it as it had when connected with the battery. (Phil. Mag. 3rd series, iv. 12.)

Faraday has applied this principle in a most happy manner to explain the phenomena of rotation discovered by Arago. If a plate of copper be revolved close to a magnetic needle suspended so that it may rotate in a plane parallel to the plate, the needle will rotate in the same direction; and, reciprocally, a rotating magnet tends to give rotation to a contiguous copper-plate. The same effects are produced by the rotation not only of all metals, but, according to Arago, of all bodies whether solid, liquid, or gaseous. These effects, which Faraday has principally examined in reference to the rotation of metals, are entirely owing to electric currents induced by the rotation, and flowing at right angles to the direction of motion.

If motion in the vicinity of a magnet induce an electric current, the same effect would be anticipated from the magnetic influence of the earth; and this fact has been proved by Faraday by most decisive and interesting experiments. When a bar of soft iron is held in the position of the dipping needle, the direction of which, in regard to terrestrial magnetism, is analogous to the axis of a common magnet, it acquires magnetic properties; and accordingly, on introducing a soft iron cylinder into a hollow helix of copper placed in the line of the dip, a galvanometer connected with the helix was instantly affected. But the use of iron may be dispensed with altogether; for when a helix of copper wire was simply moved at right angles to the dipping needle, electric currents were induced by the magnetism of the earth. The form of a helix is not even necessary: the movement of a piece of copper wire across the line of dip developed currents in the wire. The same effect was produced by the rotation of a copper plate placed horizontally so as to be nearly at right angles to the line of dip; and the revolution of a copper globe acted in the same manner. Faraday concludes that the rotation of the earth on its axis ought similarly to influence the conducting matters of its surface; and that electric currents should be thereby induced from the equatorial regions to either pole. He throws out the suggestion whether the aurora borealis and australis may not be produced by the returning currents passing from the poles of the earth into the atmosphere.

III. *Chemical Effects of Galvanism.*—The chemical agency of the voltaic apparatus, to which chemists are indebted for a most powerful instrument of analysis, was discovered by Carlisle and Nicholson, soon after the invention was made known in this country. The substance first decomposed by it was water. When two gold or platinum wires are connected with the opposite ends of a battery, and their free extremities are plunged into the same cup of water, but without touching each other, hydrogen gas is disengaged at the — and oxygen at the + wire. By collecting the gases in separate tubes as they escape, they are found to be quite pure, and in the exact ratio of two measures of hydrogen to one of oxygen. When wires of a more oxidable metal are employed, the result is somewhat different. The hydrogen gas appears as usual at the — wire; but the oxygen, instead of escaping, combines with the metal, and converts it into an oxide.

This important discovery led many able experimenters to make similar trials. Other compound bodies, such as acids and salts, were exposed to the action of galvanism, and all of them were decomposed without exception, one of their elements appearing at one side of the battery, and the other at its opposite extremity. An exact uniformity in the circumstances attending the decomposition was also remarked. Thus, in decomposing water or other compounds, the same kind of body was always disengaged at the same side of the battery. The metals, inflammable substances in general, the alkalies, earths, and the oxides of the common metals, were found at the — wire; while oxygen, chlorine, and the acids, went over to the + surface.

In performing some of these experiments, Davy observed, that if the conducting wires were plunged into separate vessels of water, made to communicate by some moist fibres of cotton or amianthus, the two gases were still disengaged in their usual order, the hydrogen in one vessel, and the oxygen in the other, just as if the wires had been immersed into the same portion of that liquid. This singular fact, and another of the like kind observed by Hisinger and Berzelius, induced him to operate in the same way with other compounds, and thus gave rise to his celebrated researches on the transfer of chemical substances from one vessel to another (Phil. Trans. 1807). In these experiments two agate cups, N and P, were employed, the first communicating with the —, the second with the + wire of the battery, and connected together by moistened amianthus. On putting a solution of sulphate of potassa or soda into N, and distilled water into P, the acid very soon passed over to the latter, while the liquid in the former, which was at first neutral, became distinctly alkaline. The process was reversed by placing the saline solution in P, and the distilled water in N, when the alkali went over to the — cup, leaving free acid in the other. That the acid in the first experiment, and the alkaline base in the second, actually passed along the amianthus, was obvious; for on one occasion, when nitrate of oxide of silver was substituted for the sulphate of potassa, the amianthus leading to N was coated with a film of metal. A similar transfer was effected by putting distilled water into N and P, and a saline solution in a third cup placed between the two others, and connected with each by moistened amianthus. In a short time the acid of the salt appeared in P, and the alkali in N. It was in pursuing these researches that Davy made his great discovery of the decomposition of the alkalies and earths, which till then had been regarded as elementary. (Phil. Trans. 1808.)

Such is a statement of the principal phenomena of electro-chemical decomposition according to the earlier experiments. The facts then observed were received as established truths of science, and passed current without suspicion or scrutiny till the present time. But Faraday, in his revision of this part of the science, has not only added much new matter, but proved that several points, which were considered as fundamental maxims, are erroneous. Before describing his results, however, I will define the new terms which he has had occasion to introduce.—In order to decompose a compound, it is necessary that it should be liquid, and that an electric current should pass through it; an object easily effected by dipping into the liquid the ends of the metallic wires which communicate with the voltaic circle. These extremities of the wires are commonly termed *poles*, from a notion of their exerting attractive and repulsive energies towards the elements of the decomposing liquid, just as the poles of a magnet act towards iron; and each is further distinguished by the term *positive* or *negative*, according as it affects an electrometer with + or — electricity. Now Faraday contends that these poles have not any attractive or repulsive energy, and act simply as a path or door to the current: he hence calls them *electrodes*, from ηλεκτρον, and ὁδος, a way. The electrodes are the surfaces, whether of air, water, metal, or any other substance, which serve to convey an electric current into and from the liquid to be decomposed. The surfaces of this liquid which are in immediate contact with the electrodes, and where the elements make their appearance, are termed *anode* and *cathode*, from *ανα*, *upwards*, and *ὅδος*, the way in which the sun rises, and *κατα*, *downwards*, the way in which the sun sets. The anode is where the + current is supposed to enter, and the cathode where it quits, the decomposing liquid, its direction, when the electrodes are placed east and west, corresponding with that of the + current which is thought to circulate on the surface of the earth (page 111). To *electrolyze* a compound, is to decompose it by the direct action of galvanism, its name being formed from *ηλεκτϱον* and *λυω*, *to unloose or set free;* and an electrolyte is a compound which may be electrolyzed. The elements of an electrolyte are called ions, from, *ιον*, going, neuter participle of the verb to go. *Anions* are the ions which appear at the anode, and are usually termed the electro-negative ingredients of a compound, such as oxygen, chlorine, and acids; and the electro-positive substances, hydrogen, metals, alkalies, which appear at the cathode, are *cations*. Whatever may be thought of the necessity for some of these terms, the words electrode, electrolyze, and electrolyte, are peculiarly appropriate, and are already in use.

The principal facts determined by Faraday may be arranged under the following propositions:—

1. All compounds, contrary to what has been hitherto supposed, are not electrolytes, that is, are not directly decomposable by an electric current. But in making this assertion it is necessary to distinguish between primary and secondary decomposition. Water is an electrolyte, its hydrogen being delivered up at the — and its oxygen at the + electrode. A solution of hydrochloric acid is likewise an electrolyte, being resolved into chlorine and hydrogen. But nitric and sulphuric acids and ammonia are not electrolytes, though the first and last are decomposed by secondary action. Thus, on subjecting nitric acid to voltaic action, the water of the solution is electrolyzed, and its hydrogen arriving at the + electrode, decomposes the nitric acid, water being there reproduced and nitrous acid formed. So, in a solution of ammonia, the oxygen of decomposed water unites at the + electrode with the hydrogen of the ammonia, and nitrogen gas is evolved. Very numerous secondary actions are occasioned in this way, because the disunited elements are presented in a nascent form, which is peculiarly favourable to chemical action; and in many instances the electrode itself, which is commonly metallic, is chemically attacked. Thus, when chlorine is evolved against an electrode of gold, oxygen at

one of some easily oxidable metal, as copper or iron, or sulphur against a silver electrode, chloride of gold, oxide of copper or iron, and sulphuret of silver, are generated. If these changes are caused by very feeble currents acting slowly, as for weeks, months, or years, the new products have opportunity to assume regularly crystalline forms. It is by such means that Becquerel has succeeded in procuring artificial minerals exactly resembling those which are found in mines (Traité d'Electricité); and Crosse has since obtained similar results (Phil. Mag. and An. ix. 229). Taking these facts in conjunction with the researches of Fox on the electrical state of mineral veins, there can be no longer a doubt that feeble electric currents within fissures of rocks, induced by terrestrial magnetism, by variations of temperature at different parts of the rock, or by the different nature of the walls of the fissures, or of the solutions with which they are filled, may have been one principal source of metalliferous deposits; nor is it at all unreasonable or unphilosophical to suppose that the enormous mineral masses which now constitute our metalliferous veins may have been the work of such feeble currents acting during hundreds or thousands of centuries. Feeble agencies operative for a long period are often just as efficacious in effecting great changes as powerful agents at work during a short period; and Becquerel, in opening this new line of inquiry, has supplied a principle by which the scientific geologist may explain many of those obscure phenomena which fall within his observation.

2. Most of the salts which have been examined are resolvable into acid and oxide, apparently without reference to their proportions. But in compounds of two elements, the ratio of combination has an influence which has hitherto been wholly overlooked. No two elements appear capable of forming more than one electrolyte. Hydrochloric acid and fused metallic protochlorides, such as the chlorides of lead and silver, and protochloride of tin, are readily decomposed; while bichloride of tin and other perchlorides resist decomposition. Substances which consist of a single equivalent of one element and two or more equivalents of some other element, are not electrolytes: this is the reason why sulphuric and nitric acid and ammonia do not yield primarily to voltaic action. This principle bids fair to become very important in determining which of several compounds of two elements contains single equivalents. Water, which is remarkable for its easy decomposition, may hence be inferred to be a true binary compound.

3. It has been ascertained that most of the elements are *ions*, and it is probable that all of them are so; but there are several important elements, such as nitrogen, carbon, phosphorus, boron, silicon, and aluminium, which have not yet been proved to be *ions*. This arises from the difficulty of obtaining these elements in compounds fitted for electrolytic action.

4. A single *ion*, that is, one ion not in combination with another, has no tendency to pass to either of the electrodes, and is quite indifferent to the passing current, unless it be itself a compound ion, and therefore electrolyzable. The character of true electrolytic action consists in the separation of *ions*, one passing to one electrode and another to the opposite electrode, and appearing there at the same instant, unless the appearance of one or both be prevented by some secondary action.

5. There is no such thing as a transfer of *ions* in the sense usually understood. In order that the elements of decomposed water should appear at the opposite electrodes, there must be water between the electrodes; and for the similar separation of sulphuric acid and soda, there must be a line of particles of sulphate of soda extending from one electrode to the other. Thus, if a solution of sulphate of magnesia be covered with pure water, care being taken to avoid all admixture of particles, and the + metallic termination or pole touch the magnesian solution only, while the — pole is in contact with the water only, a deposit of magnesia occurs just where the pure water and the magnesian solution meet, and none reaches the — pole. In Davy's experiment, where sulphuric acid and soda appeared to quit each other, and pass over separately into a vessel of pure water, there was certainly by capillary attraction an actual transfer of the salt before decomposition occurred.

6. In the foregoing experiment a surface of water acts as the — electrode, clearly showing the contact of a metallic conductor with the decomposing liquid not to be essential. Faraday has proved that even air may serve as an electrode. A current from the prime conductor of an electrical machine was made to pass from a needle's point through air to a pointed piece of litmus paper moistened with sulphate of soda, and then to issue from a similarly moistened point of turmeric paper. True electrolytic action took place, the litmus becoming red and the turmeric paper brown, though both extremities of the decomposing solution communicated solely with a stratum of air.

7. Electro-chemical decomposition cannot occur unless an electric current is actually transmitted through the electrolyte; or, in other terms, an electrolyte is always a conductor of electricity. Water, which conducts an electric current, ceases to do so when it passes into ice, and then also resists decomposition—an observation equally true of all electrolytes on becoming solid. Moreover, liquids which resist electro-chemical decomposition do not permit the current of a voltaic circle to pass. The alliance between conduction and decomposition is so constant, that the latter may be regarded as a means by which voltaic currents are transmitted through liquid compounds. Agreeably to this notion, solidity may interfere with conduction by chaining down the elements of a compound, and thereby preventing their transfer to the electrodes. Improving the conduction of a liquid, as by adding sulphuric acid to pure water, increases the decomposing power of a voltaic circle, the exciting fluid within the apparatus remaining the same; and Faraday has proved that the quantity of a compound decomposed is exactly proportional to the quantity of electricity which passes, however much other circumstances, such as the size of electrodes and conducting wires, number and size of plates, and nature of exciting fluid, may vary. Changes in these conditions do, indeed, influence the quantity of electricity transmitted; but then the degree of chemical decomposition varies in the same proportion. The foregoing facts at first led to the opinion that the current of a voltaic circle cannot pass through liquids, except those of a metallic nature, unless decomposition ensues at the same time; but Faraday has noticed that when the intensity is too feeble to effect decomposition, a small quantity of electricity may be transmitted, sufficient to be discovered by a galvanometer. This does not, however, essentially interfere with the law just announced.

8. Chemical compounds differ in the electrical force required for decomposition. A current of very feeble tension suffices to decompose iodide of potassium, while a much higher intensity is required for disuniting the elements of water. The order of easy decomposition in the annexed substances is as follows:—Solution of iodide of potassium; fused chloride of silver; fused protochloride of tin; fused chloride of lead; fused iodide of lead; solution of hydrochloric acid; and water acidulated with sulphuric acid. By extending tables of this kind, a ready method will be known for comparing the tension of voltaic circles.

9. The conduction of the electric currents within the cells of a voltaic circle depends on chemical decomposition equally with that between platinum electrodes. No substance not an electrolyte can serve to excite a voltaic apparatus; and for the passage of electricity from plate to plate through the intervening solution, the separation of substances previously combined in the required ratio is essential. Neither free oxygen nor a solution of chlorine can excite a current, though they attack the zinc and develope electricity; and in a voltaic circle excited by dilute sulphuric acid, the electricity set in motion is due to decomposed water and oxidized zinc, and not at all to the union of the oxide of zinc with sulphuric acid. The platinum electrodes and intervening liquid may be viewed as one of the cells of the circle, except that the plates act merely as conductors, without any oxidation, the current passing in virtue of the decomposed solution. In the zinc and copper cells, the current is urged on by the appetency of the zinc and oxygen to unite; whereas, in passing between the electrodes, the electricity has to surmount the mutual attraction of oxygen and hydrogen, or some similar force, without the assistance of any opposing affinity. Hence, in experiments on decomposition, the course of the electricity should be facilitated by employing large electrodes and wires, and placing them at a short distance from each other in a good conducting solution.

The principles above established show the importance of exciting all the cells of a voltaic circle with a liquid of the same strength. The electricity circulating in a voltaic apparatus with the conducting wires in contact, is equal to that which the feeblest cell is able to transmit, any chemical action in other cells more than sufficient for exciting that quantity being wasted.

THEORIES OF GALVANISM AND ELECTRO-CHEMICAL THEORY.

Of the theories proposed to account for the developement of electricity in voltaic combinations, three in particular have attracted the notice of philosophers. The first originated with Volta, who conceived that electricity is set in motion, and the supply kept up, solely by contact or communication between the metals (page 93). He regarded the interposed solutions merely as conductors, by means of which the electricity developed by each pair of plates is conveyed from one part of the apparatus to the other.

Thus, in the pile or ordinary battery, represented by the following series :—

$$+\ \overbrace{\text{zinc copper}}^{3}\quad \overset{\longleftarrow}{\text{fluid}}\quad \overbrace{\text{zinc copper}}^{2}\quad \overset{\longleftarrow}{\text{fluid}}\quad \overbrace{\text{zinc copper}}^{1}\ -$$

Volta considered that contact between the metals occasions the zinc in each pair to be +, and the corresponding copper plate to be — ; that the + zinc in each pair except the last, being separated by an intervening stratum of liquid from the — copper of the following pair, yields to it its excess of electricity; and that in this way each zinc plate communicates, not only the electricity developed by its own contact with copper, but also that which it had received from the pair of plates immediately before it. Thus, in the three pairs of plates contained in brackets, the second pair was thought to receive electricity from the first only, and the third pair from the first and second. In batteries constructed on the principle of the crown of cups (fig. 6), the *electro-motion*, as Volta called it, is ascribed to metallic communication between the zinc of one glass and the copper of the adjoining one.

The second is the *chemical theory*, proposed by Wollaston. Volta attached little importance to the chemical changes which never fail to occur in every voltaic circle, whether simple or compound, considering them as casual or unessential phenomena, and therefore neglected them in the construction of his theory. The constancy of their occurrence, however, soon attracted notice. In the earlier discussions on the cause of spasmodic movements in the frog (page 93), Fabroni contended, in opposition to Volta, that the effect was not owing to electricity at all, but to the stimulus of the metallic oxide formed or of the heat evolved during its production. More extended researches soon proved the fallacy of this doctrine; but Fabroni made a most ingenious use of the facts within his knowledge, and paved the way to the chemical theory of Wollaston.

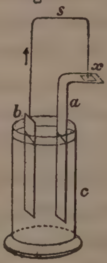
Wollaston, fully admitting electricity as the voltaic agent, assigned chemical action as the cause by which it is excited. The repetition and extension of Volta's experiments by the English chemists speedily detected the error he had committed in overlooking the chemical phenomena which occur within the pile. It was observed that no sensible effects are produced by a combination of conductors which do not act chemically on each other; that the action of the pile is always accompanied by the oxidation of the zinc; and that the energy of the pile in general is proportional to the activity with which its plates are corroded. Observations of this nature induced Wollaston to conclude that the process begins with the oxidation of the zinc,—that oxidation, or, in other terms, chemical action, was the primary cause of the developement of electricity,—that the fluid of the circle served both to oxidize the zinc and to conduct the electricity which was excited,—and that contact between the plates served only to conduct electricity, and thereby complete the circuit.

The third theory of the pile was proposed by Davy, and is intermediate between the two former. He adduced many experiments in support of Volta's statement, that the electric equilibrium is disturbed by the contact of different substances, without any chemical action taking place between them. He acknowledged, however, with Wollaston, that the chemical changes contribute to the general result; and he maintained that, though not the primary movers of the electric current, they are essential to the continued and energetic action of every voltaic circle. The electric excitement was begun, he thought, by metallic contact, and maintained by chemical action.

The progress of inquiry since these theories first came into notice, has gradually given more and more support to the views of Wollaston, and has at last, I apprehend, established it to the entire exclusion of the theory of Volta. The very fundamental position, that electricity is excitable as a primary result by the contact of different substances, is warmly contested, and, as some think with strong reason, has been disproved (page 82); but admitting, for the sake of argument, that a *small* effect, which is all that can now be contended for, may thus be produced, it is altogether insignificant when contrasted with the astonishing phenomena exhibited by a voltaic circle. The experiments of De la Rive, in reference to this question, appear irreconcilable with the theory of Volta (An. de Ch. et Ph. xxxviii. 225; lxi. 38; lxii. 147). This ingenious philosopher contends that the direction of a voltaic current is not determined by metallic contact, nor even by the nature of the metals relatively to each other, but by their chemical relation to the exciting liquid. As the result of his inquiries, he states, that of two metals composing a voltaic circle, that one which is most energetically oxidized will be + with respect to the other. Thus, when tin and copper are placed in acid solutions, the former, which is most rapidly corroded, gives a + current through the liquid to the copper, as the zinc does in the circle in fig. 1; but, if they are put into a solution of ammonia, which acts most on the copper, the direction of the current will be reversed. Copper is + in relation to lead in strong nitric acid, which oxidizes the former most freely; whereas in dilute nitric acid, by which the lead is most rapidly dissolved, the lead is +. Even two plates of copper immersed in solutions of the same acid, but of different strength, will form a voltaic circle, the plate on which chemical action is most free causing a current of + electricity to the other: nay, it is possible to construct a compound circle solely with zinc plates and one acid solution (page 95), provided the same side of each plate be more rapidly oxidized than the other.

The admirable researches of Faraday (Phil. Trans. 1833 & 34) supply conclusive evidence against the theory of Volta, proving metallic contact not to be essential to voltaic action, inasmuch as it is procured characteristically without contact. A plate of zinc, *a*, fig. 15, about 8 inches long by ½ an inch wide, was cleaned and bent at a right angle; and a plate of platinum, of the same width and 3 inches long, was soldered to a platinum wire *b s x*, the point of which, *x*, rested on a piece of bibulous paper lying upon the zinc, and moistened with a solution of iodide of potassium. On introducing the plates into a vessel, *c*, filled with dilute sulphuric and nitric acid, a + current instantly ensued in the direction of the arrow, as testified by the hydrogen evolved at the plate *a*, by the decomposed iodide of potassium, and by a galvanometer. We have thus a simple circle of the same construction and action as in figure 1, except in the absence of metallic contact.

Fig. 15.



Another proof, aptly cited by Faraday, of electric excitement being independent of contact, is afforded by the spark which appears, when the wires of a pair of plates in vigorous action are brought into contact. The spark is occasioned by the passage of electricity across a thin stratum of air; and therefore its production proves that electro-motion really occurred while the wires were yet separated by a thin stratum of air, which permitted the electric current to pass, and anterior to their actual contact.

The arrangement of figure 15, however, though good for establishing a principle, is not adapted for ordinary practice. The moist paper at *x* is a much less perfect conductor than a metal, and thus obstructs the passage of the current; nay, it does more, for it tends to establish an opposite current. In fact, on removing the dilute acid from *c*, and putting the zinc plate, *a*, in contact with the plate of platinum, an ordinary simple circle would be formed, in which a positive current would flow from the zinc at *x* through the solution to and along the wire *x s b*. This current, in Faraday's experiment, was so feeble compared with the one excited by the acid solution, that its influence was scarcely appreciable; but if the opposed currents had been of the same force, no action would have ensued.

To explain how chemical action excites electricity, recourse is had to the electro-chemical theory, first started by Davy in his essay on *Some Chemical Agencies of Electricity* (Phil. Trans. 1807). The views of Davy, which in some form or other have been adopted by most persons who have speculated on this subject, are founded on the assumption, now rendered so much more plausible than in his day, that electrical and chemical attractions are owing to one and the same agent. He considered chemical substances to be endowed with *natural electric energies;* meaning thereby, that a certain electric condition, either + or —, is natural to the atoms or combining molecules of bodies; that chemical union is the result of electrical attraction taking place between oppositely excited atoms, just as masses of matter when oppositely excited are mutually attracted; and that ordinary chemical decomposition arises from two combined atoms being drawn asunder by the electric energies of other atoms more potent than those by which they were united. Electro-chemical decomposition was at once explained by Davy on the same principles. He regarded the metallic terminations or *poles* of a voltaic circle (page 118) as two centres of electrical power, each acting repulsively to particles in the same electric state as itself, and by attraction on those which were oppositely excited. The necessary result was, that if the electric energy of the battery exceeded that by which the elements of any compound subject to its action were held together, decomposition followed, and each element was transferred bodily to the pole by which it was atttacted, passing through solutions not containing the original compound, and refusing to unite with substances for which under other circumstances it would have combined. Substances which appeared at the + pole, such as oxygen, chlorine, and acids, were termed *electro-negative* substances; and those *electro-positive* bodies, which were separated at the — pole.

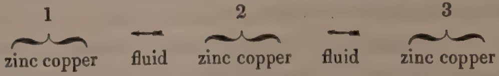
The views of Davy, both in his original essay and his subsequent explanations (Phil. Trans. 1826), were so generally and obscurely expressed, that chemists have never fully agreed, as to some points of the doctrine, about his real meaning. If he meant that a particle of free oxygen or free chlorine is in a negatively excited state, then his opinion is contrary to the fact, that neither of those gases affect an electrometer with — or any kind of electricity, any more than hydrogen gas or potassium alone exhibit any evidence of + excitement. If sulphur unites with oxygen because it has a + electric energy, why should it unite with potassium, which confessedly is far more + than itself? The only mode in which such facts as these seem reconcileable with the electro-chemical theory, is to suppose all bodies in their uncombined state to be electrically indifferent, but that they have a natural appetency to assume one state in preference to another. Electro-negative bodies are such as assume negative excitement under a certain approximation to others which at the same time become positively excited, chemical union being the consequence. On this supposition, it is intelligible that sulphur may be + in relation to oxygen, and — to potassium, just as black silk is positively electrified by friction with sealing-wax, and negatively by white silk. Accordingly, Berzelius, and others who have since speculated on this subject, have been obliged to modify the theory as first given by Davy; and it is viewed at present in different ways by different persons. The following is what appears to me most correctly to harmonise with the laws of electricity and the phenomena to be explained:— A particle of zinc and a particle of oxygen, each possessed of + and — electricity, assume in combining opposite electric conditions, and combine, in consequence of such assumption, the particles adhering together by virtue of their opposite states, just as two oppositely excited pith balls are mutually attractive. The zinc particle in becoming + gives off — electricity to the mass of zinc or other body to which it had belonged; and, in like manner, the particle of oxygen, in becoming —, supplies + electricity to adjacent particles of oxygen or other adjacent substances. Thus electro-positive bodies in the act of combining give off — electricity, and electro-negatives set free + electricity. In general, these opposite electricities instantly neutralize each other; but under favourable circumstances, as in Pouillet's experiments, such effect is prevented. So, in an experiment by De la Rive, of transmitting dry chlorine gas mixed with air through an insulated copper tube, chloride of copper is generated: if the gases pass onward in a continuous current, the + electricity set free by the chlorine is carried off by the air, while the tube is rendered negative by the — electricity lost by those particles of copper which combine with the chlorine.

Chemical decomposition also excites electricity; and by this theory it ought to do so. For a particle of zinc in quitting oxygen is +, must recover — electricity before it can resume its natural state, and in doing so leaves contiguous substances + ; and, similarly, the — oxygen renders objects — by robbing them of their + electricity. Hence, a body in combining excites in others an electric state opposite to that which it assumes ; while in the act of decomposition it produces an effect exactly the reverse.

Again, it follows from the theory, that unless the zinc can assume the + state by getting rid of — electricity, it cannot unite with oxygen ; and that chemical union will more readily ensue, the more freely a conducting medium for carrying off such — electricity is supplied. This is applicable to Davy's method of preserving copper in sea-water (page 96). A piece of zinc in contact with copper corrodes rapidly by the copper carrying off its — electricity ; while the copper thus constantly rendered —, is prevented from assuming the + state, and hence loses its power of uniting either with oxygen or chlorine. These principles readily apply to a simple voltaic arrangement, composed of zinc, copper, and dilute acid. In the broken circuit, the oxidation of the zinc causes the liquid, which supplies the oxygen, to be + ; while the zinc plate is made — by the electricity given off by the oxidizing particle of zinc. This happens whether the copper plate is present or not. The + electricity diffused in the acid solution is in part taken up by the copper plate which thereby becomes +, and is in part lost by neutralizing the — electricity on the zinc plate. In the closed circuit, the — electricity on the zinc escapes along the conducting wire to the copper plate ; the effect of which is to promote the oxidation of the zinc on the principle above stated, and by rendering the copper —, to facilitate the extraction of + electricity from the liquid. A current of + electricity thus circulates from the zinc through the liquid to the copper, and of — electricity in the opposite direction (page 94). That plate which by chemical action with the liquid excites electricity, is called the *generating plate ;* while the other is the *conducting plate*, because it performs the office of a conductor merely : in the common circle, zinc is the generating, and copper the conducting plate.

In a compound circle, represented by three pairs of plates, as in fig. 16, each pair of plates, indicated by the brackets, sends a current of + electricity from the zinc through the liquid to the copper, rendering each copper plate +, while each zinc plate is —. The first copper and second zinc plates, being oppositely electrified, neutralize each other; and the same occurs with the second copper and third zinc, as with any number of plates similarly situated. The extreme plates alone can evince an electric state, the zinc in the broken circuit being —, and the copper +; and if these plates are connected by a wire, they, like the other zinc and copper plates of the series, neutralize each other, and a continuous current is established through the whole battery, of + electricity in one direction, as shown by the arrows, and of — in the other. Thus, the quantity of electricity which circulates in one part of the closed battery, which is aptly called a *circle*, is, contrary to the notion of Volta (page 124), the same in every part (page 103). The influence of a number of plates is to augment the intensity only (page 101). This subject has been ably discussed by De la Rive. (An. de Ch. et Ph. lxii.180.)

Fig. 16.



Chemists are not agreed as to the order of electric energy in which the elements should be arranged. The following is that given by Berzelius, and may be viewed as approximative rather than rigidly exact: — Sulphur, nitrogen, and hydrogen scarcely occupy their true position in the series. The two former are less electro-negative than chlorine and fluorine, and hydrogen, I conceive, should occupy a prominent station among the electro-positive elements. All the bodies in the first series are — with regard to those in the second. In the first series each element is —, and in the second +, to all those which follow it.

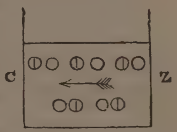
1. *Negative Electrics.*—Oxygen, sulphur, nitrogen, chlorine, iodine, fluorine, phosphorus, silenium, arsenic, chromium, molybdenum, tungsten, boron, carbon, antimony, tellurium, columbium, litanium, silicon, osmium, hydrogen.

2. *Positive Electrics.*—Potassium, sodium, lithium, barium, strontium, calcium, magnesium, glucinium, yttrium, aluminium, zirconium, manganese, zinc, cadmium, iron, nickel, cobalt, cerium, lead, tin, bismuth, uranium, copper, silver, mercury, palladium, platinum, rhodium, iridium, gold.

Theory of Chemical Decomposition.—Compounds are decomposed by galvanism, so far as is known, only when they are more or less fluid, that state being apparently necessary for giving mobility to the elements, which are otherwise chained down to one spot and prevented from separating. Davy's opinion, that an element is actually transferred beyond the place in which the decomposing compound exists, is untenable after the experiments of Faraday (page 121).

The facts adduced by the latter philosopher are inconsistent with the hypothesis of Davy, by which he accounted for chemical decomposition and transfer, namely, that attraction is exerted for the elements of compounds by the metallic conductors *a b*. The most feasible theory is that of Grotthus, of there being successive decompositions and recompositions in the line of particles lying between the electrodes. Let the upper part of fig. 17 represent a row of three particles of water lying between the electrodes *c z*, oxygen being represented by ○, and hydrogen by ⦶. A + current, in passing through them, is assumed to impart a kind of polar or magnetic virtue to the particles of oxygen and hydrogen, whereby affinity is weakened or destroyed on one side, and exalted on the other: each particle of hydrogen, for example, loses its attraction for the oxygen on its right side and quits it, but acquires an attraction for the oxygen on the left side and combines with it. Three particles of water thus yield, as in the lower part of fig. 17, two other particles which are generated; while the extreme particles of oxygen and hydrogen are set free. There is thus no transfer from one spot to another; the oxygen and hydrogen are set free at the place where they pre-existed; and they are evolved as gases, unless, by some secondary action, they should unite with the matter of the electrodes or with some element of the solution.

Fig. 17.



The preceding theoretical questions have been discussed on the assumption of electricity, as explained in the last section, being an independent principle susceptible of rapid motion from one body to another; and that the condition of a voltaic conducting wire is similar to that of a wire leading from the ground to the prime conductor of an electrical machine, or which connects the inner and outer surface of a charged Leyden phial, except that the voltaic current moves slowly, owing to its lower tension and the interposed imperfect conductor. Some conceive that what is called an electric current is not an actual transfer of anything, but a process of induction among the molecules of a conductor passing progressively along it. Others, denying independent materiality to electricity, may ascribe it to a wave of vibrating matter, just as the phenomena of optics are explained by the undulatory theory. But whatever theory of the nature of electricity may be adopted, it seems necessary, after the experiments of Faraday on the identity of voltaic and common electricity, that the nature of an electric and voltaic current is essentially the same.

PART II.

INORGANIC CHEMISTRY.

PRELIMINARY REMARKS.

In teaching a science such as chemistry, the details of which are numerous and complicated, it would be injudicious to follow the order of discovery, and proceed from individual facts to the conclusions which have been deduced from them. An opposite course is indispensable. It is necessary to discuss general principles in the first instance, in order to aid the beginner in remembering insulated facts, and in comprehending the explanations connected with them. The second part of this work will therefore commence with an explanation of the leading doctrines of the science. One inconvenience, indeed, arises from this method. It is often necessary, by way of illustration, to refer to facts of which the beginner is ignorant; and hence on some occasions more knowledge will be required for understanding a subject fully, than the reader may have at his command. But these instances will, it is hoped, be rarely met with; and when they do occur, the reader is advised to quit the point of difficulty, and return to the study of it when he shall have acquired more extensive knowledge of the details.

To the chemical history of each substance its chief physical characters will be added. A knowledge of these properties is not only advantageous in assisting the chemist to distinguish one body from another, but in many instances it is applied to uses still more important. The character called *specific gravity*, the meaning of which was explained at page 52, is of so much importance that the mode of determining it will be mentioned in this place. The process consists in weighing a body carefully, and then determining the weight of an equal bulk of water, the latter being regarded as unity. If, for example, a portion of water weigh nine grains, and the same bulk of another body 20 grains, its sp. gr. is determined by this formula;—as 9 : 20 : : 1 (assumed as the sp. gr. of water) to the fourth proportional 2·2222; so that the sp. gr. of any substance is found by dividing its weight by the weight of an equal volume of water. It is easy to discover the weight of equal bulks of water and any other liquid by filling a small bottle of known weight with each successively, and weighing them.* The method of obtaining the necessary data in case of a solid is somewhat different. The body is first weighed in air, is next suspended in water by means of a hair attached to the scale of the balance, and is then weighed again. The difference between the two weights gives the weight of a quantity of water equal to the bulk of the solid. This rule is founded on the hydrostatic law, that a solid body, immersed in any liquid, not only weighs less than it does in air, but the difference corresponds exactly to the weight of liquid which it displaces; and it is obvious that the liquid so displaced is exactly of the same dimensions as the solid. Another method is by the use of the bottle recommended for taking the sp. gr. of liquids. After weighing the bottle filled with water, a known weight of the solid is put into it, which of course displaces a quantity of water precisely equal to its own volume. The exact weight of the displaced water is found by weighing the bottle again, after its outer surface is made perfectly dry.

The determination of the sp. gr. of gaseous substances is an operation of much greater delicacy. From the extreme lightness of gases, it would be inconvenient to compare them with an equal bulk of water, and therefore atmospheric air is taken as the standard of comparison. The first step of the process is to ascertain the weight of a given volume of air. This is done by weighing a very light glass flask, furnished with a good stopcock, while full of air; and then weighing it a second time, after the air has been withdrawn by means of the air-pump. The difference between the two weights gives the information required. According to the observation of Prout, 100 cubic inches of pure and dry atmospheric air, at the temperature of 60° and when the barometer stands at 30 inches, weigh 31·0117 grains. By a similar method the weight of any other gas may be determined, and its sp. gr. be inferred accordingly. For instance, suppose 100 cubic inches of oxygen gas are found to weigh 34·109 grains, its sp. gr. will be thus deduced; as 31·0117 : 34·109 : : 1 (the sp. gr. of air) : 1·1025, the sp. gr. of oxygen.

---

* Bottles are prepared for this purpose by the philosophical instrument makers.

There are four circumstances to which particular attention must be paid in taking the specific gravity of gases:—

1. The gas should be perfectly pure, otherwise the result cannot be accurate.

2. Due regard must be had to its hygrometic condition. If it is saturated with moisture, the necessary correction may be made by the formula of page 53; or it may be dried by the use of substances which have a powerful attraction for moisture, such as chloride of calcium, quicklime, or fused potassa.

3. As the bulk of gaseous substances, owing to their elasticity and compressibility, is dependent on the pressure to which they are exposed, no two observations admit of comparison, unless made under the same elevation of the barometer. It is always understood, in taking the sp. gr. of a gas, that the barometer must stand at 30 inches, by which means the operator is certain that each gas is subject to equal degrees of compression. An elevation of thirty inches is called the standard height; and if the mercurial column be not of that length at the time of performing the experiment, the error arising from this cause must be corrected by calculation. It has been established by experiment that the bulk of gases is inversely as the pressure to which they are subject. Thus, 100 measures of air, under the pressure of 30 inches of mercury, will dilate to 200 measures, if the pressure be diminished by one half; and will be compressed to 50 measures, when the pressure is double, or equal to a mercurial column of 60 inches. The correction for the effect of pressure may therefore be made by the rule of three, as will appear by an example. If a certain portion of gas occupy the space of 100 measures at 29 inches of the barometer, its bulk at 30 inches may be obtained by the following proportion; as 30 : 29 : : 100 : 96·66.

It is understood that the temperature of the mercurial column is constant: if not so, correction must be made for the change in the volume of the mercury produced by change of temperature, on the principle laid down at page 26.

4. For a similar reason the temperature should always be the same. The standard or mean temperature is 60°; and if the gas be admitted into the weighing-flask when the thermometer is above or below that point, the formula of page 28 should be employed for making the necessary correction.

The first attempt to form a systematic chemical nomenclature was by Lavoisier, Berthollet, Guyton de Morveau, and Fourcroy, soon after the discovery of oxygen gas. To avoid an undue use of new terms, the known elements and the more familiar compound bodies were allowed to retain the names which usage had assigned to them. The newly-discovered elements were named from some striking property. Thus, oxygen, from *ὀξυς* acid, and *γενναειν* to generate, was so called from a belief that it is the universal cause of acidity; and the term hydrogen, from *ὕδωϱ* water, and *γενναειν*, was applied to the inflammable element of water. The compounds into which oxygen enters were termed *acids* or *oxides*, according as they do or do not possess acidity. The name of an acid was derived from the substance acidified by the oxygen, to which was added the termination in *ic*. Thus sulphur*ic* and carbon*ic* acids signified compounds of sulphur and carbon with oxygen. Should sulphur or any other body form two acids, the name of that containing least oxygen was made to terminate in *ous*, as sulphur*ous* acid. The termination in *uret* was applied to compounds of the simple non-metallic substances with each other, with a metal, or with a metallic oxide: thus, sulph*uret* and carb*uret* of iron signify compounds of sulphur and carbon with iron. The general term *salt* comprehended compounds of acids with alkaline bases, and the names of the salts were so contrived as to indicate the substances contained in them. If the acid contain a maximum of oxygen, the name of the salt terminated in *ate;* if a minimum, the termination in *ite* was used: thus, sulph*ate* and phosph*ate* of potassa are salts of sulphur*ic* and phosphor*ic* acids; while the terms sulph*ite* and phosph*ite* of potassa denote salts of that alkaline with sulphur*ous* and phosphor*ous* acids.

These instances suffice to exhibit the principles by which the framers of the nomenclature were guided. Their object was to apply similar names to similar things, and so to construct those names as to indicate the nature or composition of the bodies to which they were attached. The same views have been acted on by succeeding chemists, who with this intention have availed themselves of the laws of definite combination. The more essential parts of this method, as adopted in these elements, are the following:—The names of newly-discovered elements are selected from some obvious property: thus, chlorine and iodine were so called from their colour. The termination of a name is rendered similar to those of nearly allied substances: thus, iod*ine*, and fluor*ine* received that termination from their analogy to chlorine; the compounds of chlorine, iodine, bromine, and fluorine, from their relations to oxygen, are termed chlor*ides*, iod*ides*, &c.; and the compounds of selenium, and other similar inflammables, are called seleni*urets*, from their analogy to sulph*urets* and phosphurets. The names of metals, except some, as iron and tin, whose names have been sanctioned by usage, terminate in *um*, as potassium and titanium. The names of alkaline bases, when expressed by one word, terminate in *a*, as potassa and morphia. When one substance forms with oxygen three or more acids, a Greek preposition is usually prefixed to indicate the relative quantity of oxygen: thus, *hypo*nitrous acid contains less oxygen than the nitrous: *hyper*nitrous would apply to an acid with more oxygen than the nitrous; and *hypo*sulphur*ic* acid indicates an acid with less oxygen than the sulphuric, and more than the sulphurous. *Per* is sometimes prefixed with the same intention as *hyper:* thus, *per*chloric acid contains more oxygen than the chloric. Different oxides of the same metal are distinguished by derivates from the Greek or Latin. An oxide consisting of an equivalent of each element is denoted either by the term oxide without any affix, or by *prot*oxide (πρωτος, first); the highest grade is the *per*oxide; and the intermediate grades are distinguished by Latin numerals expressing the number of equivalents of oxygen combined with one equivalent of the metal, such as, *bin*oxide, *ter*oxide, &c. Sesqui, one and a half, is used to indicate the relation of 1 to $1\frac{1}{2}$, or 2 to 3, as in the Sesquioxide of iron or cobalt. The Greek numerals *dis*, *tris*, *tetrakis*, are prefixed in like manner to denote oxides formed with one equivalent of oxygen, and two, three, or more equivalents of a metal. More complex ratios, such as 3 eq. of a metal to 4 eq. of oxygen, are denoted by a fraction, $\frac{4}{3}$, placed before the name of the oxide.

The same system is extended not merely to the union of elements generally with each other, but to compounds of a more complex nature, such as the salts. To a salt formed of an equivalent of the acid and alkali, its generic name without other addition is applied; but if two or more equivalents of the acid are attached to one eq. of the base, or two or more equivalents of the base to one eq. of the acid, a numeral is prefixed so as to indicate its composition. The two salts of sulphuric acid and potassa are called sulphate and *bi*sulphate; the first containing an eq. of the acid and alkali, and the latter one eq. of the alkali to two of the acid. The three salts of oxalic acid and potassa are termed the oxalate, *bin*oxalate, and *quadr*oxalate of potassa; because one eq. of the alkali is united with one eq. of acid in the first salt, with two in the second, and with three in the third. In the chromate and *di*chromate of oxide of lead, one eq. of the acid is united with 1 eq. of oxide in the former, and with two in the latter. The term salt has of late received considerable extension, being now applied to compounds analogous to common salts in constitution, though not formed of an acid and alkali. The grounds on which this has been done, and the nomenclature introduced in consequence, are explained in the section of the salts.—In speaking of salts of metallic oxides, many chemists are in the practice, for the sake of brevity, of mentioning the name of the metals only. Thus, in the expressions *sulphates of silver and lead*, the *oxide* of silver, and *oxide* of lead, are to be understood. The present comprehensive sense in which the word *salt* is used begins to render this practice objectionable.

The generic part of the name of a compound is usually formed from that ingredient which is considered the most highly electro-negative. Thus, to compounds of oxygen and chlorine, chlorine and iodine, iodine and sulphur, sulphur and potassium, in which the first of each pair is the electro-negative element, the correct appellations are oxides of chlorine, chloride of iodine, iodide of sulphur, sulphuret of potassium; and not chloride of oxygen, iodide of chlorine, sulphuret of iodine, and potassiuret of sulphur. This practice is invariably observed in this treatise.

Convenient and philosophical as this nomenclature may at first appear, its principles are now felt to be far from coextensive with the science. It much needs extension and modification. To many of the complex compounds known to chemists it is impracticable to apply convenient names correctly expressive of their constitution; and this has led to the use of those symbolic characters which have become general among chemists, and which are essential to the present state of chemistry. The mode of employing such notation will be explained in the second section of this part.

SECTION I.

AFFINITY.

All chemical phenomena are owing to Affinity or Chemical Attraction. It is the basis on which the science of chemistry is founded. It is, as it were, the instrument which the chemist employs in all his operations, and hence it forms the first and leading object of his study.

Affinity is exerted between the minutest particles of different kinds of matter, causing them to combine so as to form new bodies endowed with new properties. It acts only at insensible distances; in other words, apparent contact, or the closest proximity, is necessary to its action. Everything which prevents such contiguity is an obstacle to combination; and any force which increases the distance between particles already combined, tends to separate them permanently from each other. In the former case, they do not come within the sphere of their mutual attraction; in the latter, they are removed out of it. It follows, therefore, that though affinity is regarded as a specific power distinct from the other forces which act on matter, its action may be promoted, modified, or counteracted by them; and consequently, in studying the phenomena produced by affinity, it is necessary to inquire into the conditions that influence its operation.

The most simple instance of the exercise of chemical attraction is afforded by the admixture of two substances. Water and sulphuric acid, or water and alcohol, combine readily. On the contrary, water shows little disposition to unite with ether, and still less with oil; for, however intimately their particles may be mixed together, they are no sooner left at rest than the ether separates almost entirely from the water, and a total separation takes place between that fluid and the oil. Sugar dissolves very sparingly in alcohol, but to any extent in water; while camphor is dissolved in a very small degree by water, and abundantly by alcohol. It appears, from these examples, that chemical attraction is exerted between different bodies with different degrees of force. There is sometimes no proof of its existence at all; between some substances it acts very feebly, and between others with great energy.

Simple combination of two substances is a common occurrence; of which the solution of salts in water, the combustion of phosphorus in oxygen gas, and the neutralization of a pure alkali by an acid, are instances. But the phenomena are often more complex. The formation of a new compound is often attended by the destruction of a pre-existing one; as when some third body acts on a compound, for one element of which it has a greater affinity than they have for one another. Thus, oil has an affinity for the volatile alkali, ammonia, and will unite with it, forming a soapy substance called a liniment. But the ammonia has a still greater attraction for sulphuric acid; and hence, if the acid be added to the liniment, the alkali will quit the oil, and unite by preference with the acid. If a solution of camphor in alcohol be poured into water, the camphor will be set free because the alcohol combines with the water. Sulphuric acid, in like manner, separates baryta from nitric acid. Combination and decomposition occur in each of these cases;—combination of sulphuric acid with ammonia, of water with alcohol, of baryta with sulphuric acid;—decomposition of the compounds formed of oil and ammonia, of alcohol and camphor, of nitric acid and baryta. These are examples of what Bergmann called *single elective affinity*;—elective, because a substance manifests, as it were, a choice for one of two others, uniting with it by preference, and to the exclusion of the other. Many of the decompositions that occur in chemistry are instances of single elective affinity.

The order in which these decompositions take place has been expressed in tables; of which the following, drawn up by Geoffroy, is an example:—

Sulphuric acid.

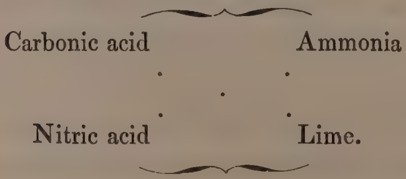
Baryta,
Strontia,
Potassa,
Soda,
Lime,
Ammonia,
Magnesia.

This table signifies, first, that sulphuric acid has an affinity for the substances placed below the horizontal line, and may unite separately with each; and, secondly, that the bases of the salts so formed will be separated from the acid by adding any of the alkalies or earths which stand above it in the column. Thus, ammonia will separate magnesia, lime ammonia, and potassa lime; but none can withdraw baryta from sulphuric acid, nor can ammonia or magnesia decompose sulphate of lime, though strontia or baryta will do so. Bergmann conceived that these decompositions are solely determined by chemical attraction, and that consequently the order of decomposition represents the comparative forces of affinity; and this view, from the simple and natural explanation it affords of the phenomenon, was for a time very generally adopted. But Bergmann was in error. It does not necessarily follow, because lime separates ammonia from sulphuric acid, that the lime has a greater attraction for the acid than the volatile alkali. Other causes are in operation which modify the action of affinity to such a degree, that it is impossible to discover how much of the effect is owing to that power. It is conceivable that ammonia may in reality have a stronger attraction for sulphuric acid than lime, and yet that the latter, from the great influence of disturbing causes, may succeed in decomposing sulphate of ammonia.

The propriety of the foregoing remark will appear from the following example:—When a stream of hydrogen gas is passed over oxide of iron heated to redness, the oxide is reduced to the metallic state, and water is generated. On the contrary, when watery vapour is brought into contact with red-hot metallic iron, the oxygen of the water quits the hydrogen and combines with the iron. It follows from the result of the first experiment, according to Bergmann, that hydrogen has a stronger attraction than iron for oxygen; and from that of the second, that iron has a greater affinity for oxygen than hydrogen. But these inferences are incompatible with each other. The affinity of oxygen for the two elements, hydrogen and iron, must either be equal or unequal. If equal, the result of both experiments was determined by modifying circumstances; since neither of these substances ought on this supposition to take oxygen from the other. But if the forces are unequal, the decomposition in one of the experiments must have been determined by extraneous causes, in direct opposition to the tendency of affinity.

The fallacy of Bergmann's opinion was detected by Berthollet. He first showed that the relative forces of chemical attraction cannot always be determined by observing the order in which substances separate each other when in combination, and that the tables of Geoffroy are merely tables of decomposition, not of affinity. He likewise traced all the various circumstances that modify the action of affinity, and gave a consistent explanation of the mode in which they operate. Berthollet went even a step further. He denied the existence of elective affinity as an invariable force, capable of effecting the perfect separation of one body from another, and maintained that all the instances of complete decomposition attributed to elective affinity are in reality determined by one or more of the collateral circumstances that influence its operation. But here this acute philosopher went too far. Bergmann erred in supposing the result of chemical action to be in every case owing to elective affinity; but Berthollet ran into the opposite extreme in declaring that the effects formerly ascribed to that power are never produced by it. That chemical attraction is exerted between bodies with different degrees of energy, is, I apprehend, indisputable. Water has a much greater affinity for hydrochloric acid and ammoniacal gases that carbonic and hydrosulphuric acids, and for these than for oxygen and hydrogen. The attraction of lead for oxygen is greater than that of silver for the same substance. The disposition of gold and silver to combine with mercury is greater than the attraction of platinum and iron for that fluid. As these differences cannot be accounted for by the operation of any modifying causes, we must admit a difference in the force of affinity in producing combination. It is equally clear that in some instances the separation of bodies from one another can only be explained on the same principle. No one, I conceive, will contend that the decomposition of hydriodic acid by chlorine, or of hydrosulphuric acid by iodine, is determined by the concurrence of any modifying circumstances.

Affinity is the cause of changes still more complicated than those which have just been considered. In a case of single elective affinity, three substances only are present, and two affinities are in play. But it frequently happens that two compounds are mixed together, and four different affinities brought into action. The changes that may or do occur under these circumstances may be studied by aid of a diagram. Thus, in mixing together a solution of carbonate of ammonia and nitrate of lime, their mutual action may be represented in the following manner:—



Each of the acids has an attraction for both bases, and hence it is possible either that the two salts should continue as they were, or that an interchange of principles should ensue, giving rise to two new compounds,—carbonate of lime and nitrate of ammonia. According to the views of Bergmann, the result is solely dependent on the comparative strength of affinities. If the affinity of carbonic acid for ammonia, and of nitric acid for lime, exceed that of carbonic acid for lime, added to that of nitric acid for ammonia, then will the two salts experience no change whatever; but if the latter affinities preponderate, then, as does actually happen in the present example, both the original salts will be decomposed, and two new ones generated. Two decompositions and two combinations take place, being an instance of what is called *double elective affinity*. Kirwan applied the terms *quiescent* and *divellent* to denote the tendency of the opposing affinities,—the action of the former being to prevent a change, the latter to produce it.

The doctrine of double elective affinity was assailed by Berthollet on the same ground and with the same success as in the case of single elective attraction. He succeeded in proving that the effect cannot always be ascribed to the sole influence of affinity. For, to take the example already adduced, if carbonate of ammonia decompose nitrate of lime by the mere force of a superior attraction, it is manifest that carbonate of lime ought never to decompose nitrate of ammonia. But if these two salts are mixed in a dry state and exposed to heat, double decomposition does take place, carbonate of ammonia and nitrate of lime being formed; and therefore, if the change in the first example was produced by chemical attraction alone, that in the second must have occurred in direct opposition to that power. It does not follow, however, because the result is sometimes determined by modifying conditions, that it must always be so. I apprehend that the decomposition of the solid cyanuret of mercury by hydrosulphuric acid gas, which takes place even at a low temperature, cannot be ascribed to any other cause than a preponderance of the divellent over the quiescent affinities.

ON THE CHANGES THAT ACCOMPANY CHEMICAL ACTION.

The leading circumstance that characterises chemical action is the loss of properties experienced by the combining substances, and the acquisition of new ones by the product of their combination. The change of property is sometimes inconsiderable. In a solution of sugar or salt in water, and in mixtures of water with alcohol or sulphuric acid, the compound retains so much of the character of its constituents, that there is no difficulty in recognising their presence. But more generally the properties of one or both of the combining bodies disappear entirely. One would not suppose from its appearance, that water is a compound body; much less that it is composed of two gases, oxygen and hydrogen, neither of which, when uncombined, has ever been compressed into a liquid. Hydrogen is one of the most inflammable substances in nature, and yet water cannot be set on fire: oxygen, on the contrary, enables bodies to burn with great brilliancy, and yet water extinguishes combustion. The alkalies and earths were regarded as simple till Davy proved them to be compound; and certainly they evince no sign whatever of containing oxygen and a metal. Numerous examples of a similar kind are afforded by the mutual action of acids and alkalies. Sulphuric acid and potassa, for example, are highly caustic. The former is intensely sour, reddens the blue colour of vegetables, and has a strong affinity for alkaline substances; the latter has a pungent taste, converts the blue colour of vegetables to green, and combines readily with acids. On adding these principles cautiously to each other, a compound results called a *neutral salt*, which does not in any way affect the colouring matter of plants, and in which the other distinguishing features of the acid and alkali can no longer be perceived. They appear to have destroyed the properties of each other, and are hence said to *neutralize* one another.

The other phenomena that accompany chemical action are changes of density, temperature, form, and colour.

1. It is observed that two bodies rarely occupy, after combination, the same space which they possessed separately. In general their bulk is diminished, so that the sp. gr. of the new body is greater than the mean of its components. Thus a mixture of 100 measures of water and an equal quantity of sulphuric acid does not occupy the space of 200 measures, but considerably less. A similar contraction frequently attends the combination of solids. Gases often experience a remarkable condensation when they unite. The elements of olefiant gas, for instance, would expand to four times the bulk of that compound, if they were suddenly to become free, and assume the gaseous form. But the rule is not without exception. The reverse happens in some metallic compounds;

and there are examples of combination between gases without any change of bulk.

2. A change of temperature generally accompanies chemical action. Heat is evolved either when there is a diminution in the bulk of the combining substances without change of form, or when a gas is condensed into a liquid, or a liquid becomes solid. The heat caused by mixing sulphuric acid with water is an instance of the former; and the common process of slaking lime, during which water loses its liquid form in combining with that earth, is an example of the latter. The rise of temperature in these cases is obviously referable to diminished sp. heat in the new compound; but intense heat sometimes accompanies chemical action under circumstances in which an explanation founded on a change of sp. heat is inadmissible. At present it is enough to have stated the fact; its theory will be discussed under the subject of combustion. The production of cold seldom or never takes place during combination, except when heat is rendered insensible by the conversion of a solid into a liquid, or a liquid into a gas. All the frigorific mixtures act in this way.

3. The changes of form that attend chemical action are exceedingly various. The combination of gases may give rise to a liquid or a solid; solids sometimes become liquid, and liquids solid. Several familiar chemical phenomena, such as detonation, effervescence, and precipitation, are owing to these changes. The sudden evolution of a large quantity of gaseous matter causes an explosion, as when gunpowder detonates. The slower disengagement of gas produces effervescence, as when marble is put into hydrochloric acid. A precipitate is owing to the formation of a new body which happens to be insoluble in the liquid in which its elements were dissolved.

4. Chemical action is frequently attended by change of colour. No uniform relation has been traced between the colour of a compound and that of its elements. Iodine, whose vapour is of a violet hue, forms a beautiful red compound with mercury, and a yellow one with lead. The black oxide of copper generally gives rise to green and blue coloured salts; while the salts of the oxide of lead, which is itself yellow, are for the most part colourless. The colour of precipitates is a very important study, as it supplies a character by which most substances may be distinguished.

ON THE CIRCUMSTANCES THAT MODIFY AND INFLUENCE THE OPERATION OF AFFINITY.

Of the conditions which are capable of promoting or counteracting the tendency of chemical attraction, the following are the most important: cohesion, elasticity, quantity of matter, gravity, and contact with other bodies. To these may be added the agency of the imponderables.

Cohesion.—The first obvious effect of cohesion is to oppose affinity, by impeding or preventing that mutual penetration and close proximity of the particles of different bodies, which is essential to the successful exercise of their attraction. Bodies seldom act chemically in their solid state; their molecules do not come within the sphere of attraction, and therefore combination cannot take place, although their affinity may in fact be considerable. Liquidity, on the contrary, favours chemical action; it permits the closest possible approximation, while the cohesive power is comparatively so trifling as to oppose no appreciable barrier to affinity.

Cohesion may be diminished in two ways, — by mechanical division, or by the application of heat. The former aids by increasing the extent of surface; but it is not of itself in general sufficient, because the particles, however minute, still retain that degree of cohesion which constitutes solidity. Heat acts with greater effect, and never fails in promoting combination, whenever the cohesive power is a barrier to it. Its intensity should always be so regulated as to produce liquefaction. The fluidity of one of the substances frequently suffices for effecting chemical union, as is proved by the facility with which water dissolves many salts and other solid bodies. But the cohesive force is still in operation; for a solid is commonly dissolved in greater quantity when its cohesion is diminished by heat. The reduction of both substances to the liquid state is the best method for ensuring chemical action. The slight degree of cohesion possessed by liquids does not appear to cause any impediment to combination; for they commonly act as energetically on each other at low temperatures, or at a temperature just sufficient to cause perfect liquefaction, as when their cohesive power is still further diminished. It seems fair to infer, therefore, that very little, if any, affinity exists between two bodies which do not combine when they are intimately mixed in a liquid state.

The phenomena of crystallization are owing to the ascendency of cohesion over affinity. When a large quantity of salt has been dissolved in water by the aid of heat, part of the saline matter generally separates as the solution cools, because the cohesive power of the salt then becomes comparatively too powerful for chemical attraction. Its particles begin to cohere together, and are deposited in crystals, the process of crystallization continuing till it is arrested by the affinity of the liquid. A similar change happens when a solution made in the cold is gradually evaporated. The cohesion of the saline particles is no longer counteracted by the affinity of the liquid, and the salt therefore assumes the solid form.

Cohesion plays a still more important part. It sometimes determines the result of chemical action, probably even in opposition to affinity. Thus, on mixing together a solution of two acids and one alkali, of which two salts may be formed, one soluble and the other insoluble, the alkali will unite with that acid with which it forms the insoluble compound, to the total exclusion of the other. This is one of the modifying circumstances employed by Berthollet to account for the phenomena of single elective attraction, and is certainly applicable to many of the instances to be found in the tables of affinity. When, for example, hydrochloric acid, sulphuric acid, and baryta are mixed together, sulphate of baryta is formed in consequence of its insolubility. Lime, which yields an insoluble salt with carbonic acid, separates that acid from ammonia, potassa, and soda, with all of which it makes soluble compounds.

A similar explanation may be given of many cases of double elective attraction. On mixing together in solution four substances, A, B, C, D, of which it is possible to form four compounds, AB and CD, or AC and BD, that compound will certainly be produced which happens to be insoluble. Thus, sulphuric acid, soda, nitric acid, and baryta may give rise either to sulphate of soda and nitrate of baryta, or to sulphate of baryta and nitrate of soda; but the first two salts cannot exist together in the same liquid, because the insoluble sulphate of baryta is instantly generated, and its formation necessarily causes the nitric acid to combine with the soda. In like manner, a solution of nitrate of lime is decomposed by carbonate of ammonia, in consequence of the insolubility of carbonate of lime.

To comprehend the manner in which cohesion acts in these instances, it is necessary to consider what takes place when in the same liquid two or more compounds are brought together, which do not give rise to an insoluble substance. Thus, on mixing solutions of sulphate of potassa and nitrate of soda, no precipitate ensues; because the salts capable of being formed by double decomposition, sulphate of soda and nitrate of potassa, are likewise soluble. In this case it is possible either that each acid may be confined to one base, so as to constitute two neutral salts; or that each acid may be divided between both bases, yielding four neutral salts. It is difficult to decide this point in an unequivocal manner: but, judging from many chemical phenomena, there can, I apprehend, be no doubt that the arrangement last mentioned is the most frequent, and is probably universal whenever the relative forces of affinity are not very unequal. When two acids and two bases meet together in neutralizing proportion, it may therefore be inferred, that each acid unites with both the bases in a manner regulated by their respective forces of affinity, and that four salts are contained in solution. In like manner, the presence of three acids and three bases will give rise to nine salts; and when four of each are present, sixteen salts will be produced. This view affords the most plausible theory of the constitution of mineral waters, and of the products which they yield by evaporation.

The influence of insolubility in determining the result of chemical action may be readily explained on this principle. If nitric acid, sulphuric acid, and baryta are mixed together in solution, the base may be conceived to be at first divided between the two acids, and nitrate and sulphate of baryta to be generated. The latter, being insoluble, is instantly removed beyond the influence of the nitric acid, so that for an instant nitrate of baryta and free sulphuric acid remain in the liquid: but as the base left in solution is again divided between the two acids, a fresh quantity of the insoluble sulphate is generated; and this process of partition continues, until either the baryta or the sulphuric acid is withdrawn from the solution. Similar changes ensue when nitrate of baryta and sulphate of soda are mixed.

The separation of salts by crystallization from mineral waters or other saline mixtures is explicable by a similar mode of reasoning. Thus, on mixing nitrate of potassa and sulphate of soda, four salts, according to this view, are generated,—namely, the sulphates of soda and potassa, and the nitrates of those bases; and if the solution be allowed to evaporate gradually, a point at length arrives when the least soluble of these salts, the sulphate of potassa, will be disposed to crystallize. As soon as some of its crystals are deposited, and thus withdrawn from the influence of the other salts, the constituents of these undergo a new arrangement, whereby an additional quantity of sulphate of potassa is generated; and this process continues until the greater part of the sulphuric acid and potassa has combined, and the compound is removed by crystallization. If the difference in solubility is considerable, the separation of salts may be often rendered very complete by this method.

The efflorescence of a salt is sometimes attended with a similar result. If carbonate of soda and chloride of calcium are mingled together in solution, the insoluble carbonate of lime subsides. But if carbonate of lime and sea-salt are mixed in the solid state, and a certain degree of moisture is present, carbonate of soda and chloride of calcium are slowly generated; and since the former, as soon as it is formed, separates itself from the mixture by efflorescence, its production continues progressively. The efflorescence of carbonate of soda, which is sometimes seen on old walls, or which in some countries is found on the soil, appears to have originated in this manner.

Elasticity.—From the obstacle which cohesion puts in the way of affinity, the gaseous state, in which the cohesive power is wholly wanting, might be expected to be peculiarly favourable to chemical action. The reverse, however, is the fact. Bodies evince little disposition to unite when presented to each other in the elastic form. Combination does indeed sometimes take place, in consequence of a very energetic attraction; but examples of an opposite kind are much more common. Oxygen and hydrogen gases, and chlorine and hydrogen, though their mutual affinity is very powerful, may be preserved together for any length of time without combining. This want of action seems to arise from the distance between the particles preventing that close approximation which is so necessary to the successful exercise of affinity. Hence many gases cannot be made to unite directly, which nevertheless combine readily while in their *nascent* state; that is, while in the act of assuming the gaseous form by the decomposition of some of their solid or fluid combinations.

Elasticity operates likewise as a decomposing agent. If two gases, the reciprocal attraction of which is feeble, suffer considerable condensation when they unite, the compound will be decomposed by very slight causes. Chloride of nitrogen, which is an oil-like liquid, composed of the two gases chlorine and nitrogen, affords an apt illustration of this principle, being distinguished for its remarkable facility of decomposition. Slight elevation of temperature, by increasing the natural elasticity of the two gases, or contact of substances which have an affinity for either of them, produces immediate explosion.

Many familiar phenomena of decomposition are owing to elasticity. All compounds that contain a volatile and a fixed principle are liable to be decomposed by a high temperature. The expansion occasioned by heat removes the elements of the compound to a greater distance from each other, and thus, by diminishing the force of chemical attraction, favours the tendency of the volatile principle to assume the form which is natural to it. The evaporation of water from a solution of salt is an instance of this kind.

Many solid substances which contain water in a state of intimate combination part with it in a strong heat, in consequence of the volatile nature of that liquid. The separation of oxygen from some metals, by heat alone, is explicable on the same principle.

From these and some preceding remarks, it appears that the influence of heat over affinity is variable; for at one time it promotes chemical union, and opposes it at another. Its action, however, is always consistent. Whenever the cohesive power is an obstacle to combination, heat favours affinity either by diminishing the cohesion of a solid, or by converting it into a liquid. As the cause of the gaseous state, on the contrary, it keeps at a distance particles which would otherwise unite; or, by producing expansion, it tends to separate from one another substances which are already combined. There is one effect of heat which seems somewhat anomalous; namely, the combination which ensues in gaseous explosive mixtures on the approach of flame. The explanation given by Berthollet is probably correct,—that the sudden dilatation of the gases in the immediate vicinity of the flame acts as a violent compressing power to the contiguous portions, and thus brings them within the sphere of their attraction.

Some of the decompositions, which were attributed by Bergmann to the sole influence of elective affinity, may be ascribed to elasticity. If three substances are mixed together, two of which can form a compound which is less volatile than the third, the last will, in general, be completely driven off by the application of heat. The decomposition of the salts of ammonia by the pure alkalies or alkaline earths may be adduced as an example; and, for a like reason, all the carbonates are decomposed by nitric acid, and all the nitrates by sulphuric acid. This explanation applies equally well to some cases of double decomposition. It explains, for instance, why dry carbonate of lime will decompose nitrate of ammonia by the aid of heat; for carbonate of ammonia is more volatile than the nitrate either of ammonia or lime.

The influence of elasticity in determining the result of chemical action in these instances seems owing to the same cause which enables insolubility to be productive of similar effects. Thus, on mixing nitrate of ammonia with lime, the acid is divided between the two bases; some ammonia becomes free, which, in consequence of its elasticity, is entirely expelled by a gentle heat. The acid of the remaining nitrate of ammonia is again divided between the two bases; and if a sufficient quantity of lime is present, the ammoniacal salt will be completely decomposed. In like manner, the decomposition of potassa may be effected by iron, though the affinity of this metal for oxygen seems much inferior to that of potassium for oxygen. If potassa in the fused state be brought in contact with metallic iron at a white heat, the oxygen is divided between the two metals, and a portion of potassium set at liberty. But as potassium is volatile at a white heat, it is expelled at the instant of reduction; and thus, by its influence being withdrawn, an opportunity is given for the decomposition of an additional quantity of potassa.

Quantity of Matter.—The influence of quantity of matter over affinity is universally admitted. If one body, A, unites with another, B, in several proportions, that compound will be most difficult of decomposition which contains the smallest quantity of B. Of the three oxides of lead, for instance, the peroxide parts most easily with its oxygen by the action of heat; a higher temperature is required to decompose the red oxide; and the protoxide will bear the strongest heat of our furnaces without losing a particle of its oxygen.

The influence of quantity over chemical attraction may be further illustrated by the phenomena of solution. When equal weights of a soluble salt are added in succession to a given quantity of water, which is capable of dissolving almost the whole of the salt employed, the first portion of the salt will disappear more readily than the second, the second than the third, the third than the fourth, and so on. The affinity of the water for the saline substance diminishes with each addition, till at last it is so weakened as to be unable to overcome the cohesion of the salt. The process then ceases, and a saturated solution results.

Quantity of matter is employed advantageously in many chemical operations. If a chemist wishes to displace a metallic oxide from an acid by the superior affinity of potassa for the latter, he frequently uses rather more of the alkali than is sufficient for neutralizing the acid. He employs an excess of the alkali, in order the more effectually to bring every particle of the substance to be decomposed in contact with the decomposing agent.

But Berthollet has attributed much greater influence to quantity of matter. It was the basis of his doctrine, developed in the *Statique Chimique*, that bodies cannot be wholly separated from each other by the affinity of a third substance for one element of a compound; and to explain why a superior chemical attraction does not produce the effect which might be expected from it, he contended that quantity of matter compensates for a weaker affinity. From the co-operation of several disturbing causes, Berthollet perceived that the force of affinity cannot be estimated with certainty by observing the order of decomposition; and he therefore had recourse to another method. He supposed the affinity of different acids for the same alkali to be in the inverse ratio of the ponderable quantity of each which is necessary for neutralizing equal quantities of the alkali. Thus, if two parts of one acid, A, and one part of another acid, B, are required to neutralize equal quantities of the alkali, C, it was inferred that the affinity of B for C was twice as great as that of A. He conceived, further, that as two parts of A produce the same neutralizing effect as one part of B, the attraction exerted by any alkali towards two parts of A ought to be precisely the same as for the one part of B; and he hence concluded that there is no reason why the alkali should prefer the small quantity of one to the large quantity of the other. On this he founded the principle that quantity of matter compensates for force of attraction.

Berthollet has here obviously confounded two things, namely, force of attraction and neutralizing power, which are really distinct. The relative weights of hydrochloric and sulphuric acids required to neutralize an equal quantity of any alkali, or, in other words, their capacities of saturation, are as 36·4 to 40, a ratio which remains constant with respect to all other alkalies. The affinity of these acids, according to Berthollet's rule, will be expressed by the inverse ratio of these numbers. But in taking this estimate, we have to make three assumptions, each of which is disputable. There is no proof, in the first place, that hydrochloric acid has a greater affinity for an alkali, such as potassa, than sulphuric acid. Such an inference would be directly opposed to the general opinion founded on the order of decomposition; and though that order, as we have shown, is by no means a satisfactory test of the strength of affinity, it would be improper to adopt an opposite conclusion without having good reasons for so doing. Secondly, were it established that hydrochloric acid has the greater affinity, it does not follow that the attraction of those acids for potassa is in the inverse ratio of 36·4 to 40. And, thirdly, supposing this point settled, it is very improbable that the ratio of their affinities for one alkali will apply to all others; analogy would lead us to anticipate the reverse. Independently of these objections, Dulong has found that the principle of Berthollet is not in accord with the results of experiment.

Gravity.—The influence of gravity is perceptible when it is wished to make two substances unite, the densities of which are different. In a case of simple solution, a larger quantity of saline matter is found at the bottom than at the top of the liquid, unless the solution shall have been well mixed subsequently to its formation. In making an alloy of two metals which differ in density, a larger quantity of the heavier metal will be found at the lower than in the upper part of the compound, unless great care be taken to counteract the tendency of gravity by agitation. This force obviously acts, like the cohesive power, in preventing a sufficient degree of approximation.

Contact with other bodies.—The influence of contact of different substances in modifying affinity is observable either in the increased or diminished energy of chemical action. The former is always the result of a galvanic current, and has been treated of elsewhere: the latter is produced by the interposition of an indifferent body by which others are removed out of the sphere of their mutual action. Thus, on immersing a fragment of pure zinc into dilute sulphuric acid the chemical action is no sooner commenced than it is checked by the hydrogen which is liberated; this is effected by the minute globules of the gas collecting upon the surface of the zinc, and adhering firmly to it, preventing the zinc and dilute acid from coming into that close contact which is essential to chemical action. Some means must therefore be used to remove this intervening film of hydrogen, if a continuous action be desired: this is effected when the common zinc of commerce is used by the minute portions of other metals present in it as impurities, by which small but numerous galvanic currents are excited, and by their action the hydrogen is collected and makes its escape as globules of gas.

Imponderables.—The influence which heat exerts over chemical phenomena, and the modes in which it operates, have been already discussed. The chemical agency of galvanism has also been described. The effects of light will be most conveniently stated in other parts of the work. Electricity is frequently employed to produce the combination of gases with one another, and in some instances to separate them. It appears to act by the heat which it occasions, and therefore on the same principle as flame.

On the measure of affinity.—As the foregoing observations prove that the order of decomposition is not always a satisfactory measure of affinity, it becomes a question whether there are any means of determining the comparative forces of chemical attraction. When no disturbing causes operate, the phenomena of decomposition afford a sure criterion; but when the conclusions obtained in this way are doubtful, assistance may be frequently derived from other sources. The surest indications are procured by observing the tendency of different substances to unite with the same body under the same circumstances, and subsequently marking the comparative facility of decomposition when the compounds so formed are exposed to the same decomposing agent. Thus, on exposing silver, lead, and iron, to air and moisture, the iron soon rusts, the lead is oxidized in a slight degree only, and the silver resists oxidation altogether. Iron is hence inferred to have the greatest affinity for oxygen, lead next, and silver the least. This conclusion is supported by concurring observations of a like nature, and confirmed by the circumstances under which the oxides of those metals part with their oxygen. Oxide of silver is reduced by heat only; and oxide of lead is decomposed by charcoal at a lower temperature than oxide of iron.

It is inferred from the action of heat on the carbonate of potassa, baryta, lime, and oxide of lead, that potassa has a stronger attraction for carbonic acid than baryta, baryta than lime, and lime than oxide of lead. The affinity of different substances for water may be determined in a similar manner.

Of all chemical substances, our knowledge of the relative degrees of attraction of acids and alkalies for each other is the most uncertain. Their mutual action is affected by so many circumstances, that it is in most cases impossible, with certainty, to refer any effect to its real cause. The only methods that have been hitherto devised for remedying this defect are those of Berthollet and Kirwan. Both are founded on the capacities of saturation, and the objections which have been urged to the rule suggested by the former philosopher apply equally to that proposed by the latter. But this uncertainty is of no great consequence in practice. We know perfectly the order of decomposition, whatever may be the actual forces by which it is effected.

SECTION II.

ON THE PROPORTIONS IN WHICH BODIES UNITE, AND ON THE LAWS OF COMBINATION.

The study of the proportions in which bodies unite naturally resolves itself into two parts. The first includes compounds whose elements appear to unite in a great many proportions; the second comprehends those, the elements of which combine in a few proportions only.

I. The compounds contained in the first division are of two kinds. In one, combination takes place unlimitedly in all proportions; in the other, it occurs in every proportion within a certain limit. The union of water with alcohol and the liquid acids, such as the sulphuric, hydrochloric, and nitric, affords instances of the first mode of combination; the solutions of salts in water are examples of the second. One drop of sulphuric acid may be diffused through a gallon of water, or a drop of water through a gallon of the acid; or they may be mixed together in any intermediate proportions; and nevertheless in each case they appear to unite perfectly with each other. A hundred grains of water, on the contrary, will dissolve any quantity of sea-salt which does not exceed forty grains. Its solvent power then ceases, because the cohesion of the solid becomes comparatively too powerful for the force of affinity. The limit to combination is in such instances owing to the cohesive power; and but for the obstacle which it occasions, the salt would most probably unite with water in every proportion.

All substances that unite in many proportions, give rise to compounds which have this common character, that their elements are united by a feeble affinity, and preserve, when combined, more or less of the properties which they possess in a separate state. In a scientific point of view, these combinations are of a minor importance: but they are exceedingly useful as instruments of research. They enable the chemist to present bodies to each other, under circumstances peculiarly favourable for acting with effect: the liquid form is thus communicated to them; while the affinity of the solvent or menstruum, which holds them in solution, is not sufficiently powerful to interfere with their mutual attraction.

II. The most interesting series of compounds is produced by substances which unite in a few proportions only; and which, in combining, lose more or less completely the properties that distinguished them when separate. Of these bodies, some form but one combination. Thus there is only one compound of boron and oxygen, and of chlorine and hydrogen. Others combine in two proportions. For example, two compounds are formed by tin and oxygen, and by hydrogen and oxygen. Other bodies again unite in three, four, five, or even six proportions, which is the greatest number of compounds that any two substances are known to produce, except perhaps carbon and hydrogen, and those which belong to the first division.

The combination of substances that unite in a few proportions only, is regulated by the three following remarkable laws:—

1. The First of these Laws is, that the composition of bodies is fixed and invariable. A compound substance, so long as it retains its characteristic properties, always consists of the same elements united together in the same proportion. Sulphuric acid, for example, is always composed of sulphur and oxygen in the ratio of 16 parts of the former to 24 of the latter: no other elements can form it, nor can it be produced by its own elements in any other proportion. Water, in like manner, is formed of 1 part of hydrogen and 8 of oxygen; and were these elements to unite in any other ratio, some new compound, different from water, would be the product. The same observation applies to all other substances, however complicated, and at whatever period they were produced. Thus sulphate of baryta, whether formed ages ago by the hand of nature, or quite recently by the operations of the chemist, is always composed of 40 parts of sulphuric acid and 76·7 of baryta. This law, in fact, is universal and permanent. Its importance is equally manifest: it

is the essential basis of chemistry, without which the science itself could have no existence.

Two views have been proposed by way of accounting for this law. The explanation now universally given is confined to a mere statement, that substances are disposed to combine in those proportions to which they are so strictly limited, in preference to any others; it is regarded as an ultimate fact, because the phenomena are explicable on no other known principle. A different doctrine was advanced by Berthollet, in his *Statique Chimique*, published in 1803. Having observed the influence of cohesion and elasticity in modifying the action of affinity as already described, he thought he could trace the operations of the same causes in producing the effect at present under consideration. As the solubility of a salt and of a gas in water is limited, in the former by cohesion, in the latter by elasticity, he conceived that the same forces would account for the unchangeable composition of certain compounds. He maintained that within certain limits bodies have a tendency to unite in every proportion; and that combination is never definite and invariable, except when rendered so by the operation of modifying causes, such as cohesion, insolubility, elasticity, quantity of matter, and the like. Thus, according to Berthollet, sulphate of baryta is composed of 40 parts of sulphuric acid and 76·7 of baryta, not because those substances are disposed to unite in that ratio rather than in another, but because the compound so constituted happens to have great cohesive power.

These opinions were ably and successfully combated by Proust in several papers published in the *Journal de Physique*, wherein he proved that the metals are disposed to combine with oxygen and with sulphur only in one or two proportions, which are definite and invariable; and a controversy ensued remarkable for the moderation with which it was conducted on both sides. The question is now no longer at issue. The great variety of facts, similar to those observed by Proust, which have since been established, has proved beyond a doubt that the leading principle of Berthollet is erroneous. The tendency of bodies to unite in definite proportions only, is indeed so great as to excite a suspicion that all substances combine in this way; and that the exceptions thought to be afforded by the phenomena of solution, are rather apparent than real; for it is conceivable that the apparent variety of proportion, noticed in such cases, may arise from the mixture or combination of a few definite compounds with each other.

2. The Second Law of Combination is, that the relative quantities in which bodies unite, may be expressed by proportional numbers. Thus, 8 parts of oxygen united with 1 part of hydrogen, 16 of sulphur, 35·4 of chlorine, 39·6 of selenium, and 108 parts of silver. Such are the quantities of these five bodies which are disposed to unite with 8 parts of oxygen; and it is found that when they combine with one another, they unite either in the proportions expressed by those numbers, or in multiples of them according to the third law of combination. Hydrosulphuric acid, for instance, is composed of 1 part of hydrogen and 16 of sulphur, and bisulphuret of hydrogen of 1 part of hydrogen to 32 of sulphur; 35·4 of chlorine unite with 1 of hydrogen, 16 of sulphur, and 108 of silver; and 39·6 parts of selenium with 1 of hydrogen, and sixteen of sulphur.

From the occurrence of such proportional numbers has arisen the use of certain terms, as *Proportion*, *Combining Proportion*, *Proportional*, and *Chemical Equivalent*, or *Equivalent*, to express them. The latter term, introduced by Wollaston, and which is employed in this treatise, was suggested by the circumstance that the combining proportion of one body is, as it were, *equivalent* to that of another body, and may be substituted for it in combination. Among the tables at the end of the volume will be found one of the equivalents of elementary substances.

This law is not confined to elementary substances, since compound bodies have their combining proportions or equivalents, which may likewise be expressed in numbers. Thus, since water is composed of 1 eq. or 8 parts of oxygen, and 1 eq. or 1 of hydrogen, its combining proportion or equivalent is 9. The equivalent of sulphuric acid is 40, because it is a compound of one eq. or 16 parts of sulphur, and three eq. or 24 parts of oxygen; and in like manner, the eq. of hydrochloric acid is 36·4, because it is a compound of one eq. or 35·4 parts of chlorine, and one eq. or 1 part of hydrogen. The equivalent number of potassium is 39, and as that quantity combines with 8 of oxygen to form potassa, the equivalent of the latter is $39 + 8 = 47$. Now when these compounds unite, one equivalent of the one combines with one, two, three, or more equivalents of the other, precisely as the simple substances do. Hydrate of potassa, for example, is constituted of 47 parts of potassa and 9 of water, and its equivalent is consequently $47 + 9$, or 56. Sulphate of potassa is composed of 40 sulphuric acid + 47 potassa; and the nitrate of that alkali of 54 nitric acid + 47 of potassa.

The equivalent of the former salt is therefore 87, and of the latter 101.

The composition of the salts affords a very instructive illustration of this subject; and to exemplify it still further, a list of the equivalents of a few acids and alkaline bases is annexed:—

Hydrofluoric Acid	19·7	Lithia	14
Phosphoric Acid	35·7	Magnesia	20·7
Hydrochloric	36·4	Lime	28·5
Sulphuric Acid	40·1	Soda	31·3
Nitric Acid	54·15	Potassa	47·15
Arsenic Acid	57·7	Strontia	51·8
Selenic Acid	63·6	Baryta	76·7

The alkalies are here shown to differ widely in neutralizing power; for the equivalent of each base expresses the quantity required to neutralize an equivalent of each of the acids. Thus 14 of lithia, 31·3 of soda, and 76·7 of baryta, combine with 54·15 of nitric acid, forming the neutral nitrates of lithia, soda, and baryta. The same fact is obvious with respect to the acids; for 40·1 of sulphuric, 54·15 of nitric, and 63·6 of selenic acid unite with 76·7 of baryta, forming a neutral sulphate, nitrate and selenate of baryta.

These circumstances afford a ready explanation of a curious fact, first noticed by the Saxon chemist Wenzel; namely, that when two neutral salts mutually decompose each other, the resulting compounds are likewise neutral. The cause of this fact is now obvious. If 71·3 parts of neutral sulphate of soda are mixed with 130·7 of nitrate of baryta, the 76·7 parts of baryta unite with 40 of sulphuric acid, and the 54 parts of nitric acid of the nitrate combine with the 31·3 of soda of the sulphate, not a particle of acid or alkali remaining in an uncombined condition.

Sulphate of Soda.		Nitrate of Baryta.	
Sulphuric acid	40	54	Nitric acid.
Soda	31·3	76·7	Baryta
	71·3	130·7	

It matters not whether more or less than 71·3 parts of sulphate of soda are added; for if more, a small quantity of sulphate of soda will remain in solution; if less, nitrate of baryta will be in excess; but in either case the neutrality will be unaffected.

3. The Third Law of Combination is, that when one body, A, unites with another body, B, in two or more proportions, the quantities of the latter, united with the same quantity of the former,

bear to each other a very simple ratio. The progress of chemical research, in discovering new compounds and ascertaining their exact composition, has shown that these ratios of B may be represented by one or other of the two following series:—

1st Series. A unites with 1, 2, 3, 4, 5, &c. of B.

2nd Series. A unites with 1, 1½, 2, 2½, &c. of B.

The first series is exemplified by the subjoined compounds.

Water is composed of	Hydrogen	1	Oxygen	8	1
Binoxide of Hydrogen	Do.	1	Do.	16	2
Carbonic Oxide	Carbon	6	Do.	8	1
Carbonic Acid	Do.	9	Do.	16	2
Nitrous Oxide	Nitrogen	14·15	Do.	8	1
Nitric Oxide	Do.	14·15	Do.	16	2
Hyponitrous Acid	Do.	14·15	Do.	24	3
Nitrous Acid	Do.	14·15	Do.	32	4
Nitric Acid	Do.	14·15	Do.	40	5

In all these compounds the ratio of the oxygen are expressed by whole numbers. In water the hydrogen is combined with half as much oxygen as in the binoxide of hydrogen, so that the ratio is as 1 to 2. The same relation holds in carbonic oxide and carbonic acid. The oxygen in the compounds of nitrogen and oxygen is in the ratio of 1, 2, 3, 4, and 5. In like manner the ratio of sulphur in the two sulphurets of mercury, and that of chlorine in the two chlorides of mercury, is as 1 to 2. So, in bicarbonate of potassa, the alkali is united with twice as much carbonic acid as in the carbonate; and the acid of the three oxalates of potassa is in the ratio of 1, 2, and 4.

The following compounds exemplify the second series:—

Protoxide of Iron	consists of Iron	28	Oxygen	8	1
Peroxide	Do.	28	Do.	12	1½
Protoxide of Manganese	Manganese	27·7	Do.	8	1
Sesqui-oxide	Do.	27·7	Do.	12	1½
Bin-oxide	Do.	27·7	Do.	16	2
Arsenious Acid	Arsenic	37·7	Do.	12	1½
Arsenic Acid	Do.	37·7	Do.	20	2½
Hypophosphorous Acid	Phosphorus	15·7	Do.	4	½
Phosphorous Acid	Do.	15·7	Do.	12	1½
Phosphoric Acid	Do.	15·7	Do.	20	2½

Both of these series, which together constitute the Third Law of Combination, result naturally from the operation of the second law. The first series arises from one equivalent of a body uniting with 1, 2, 3, or more equivalents of another body. The second series is a consequence of two equivalents of one substance combining with 3, 5, or more equivalents of another. Thus, if two equivalents of phosphorus unite both with 3 and with 5 equivalents of oxygen, we obtain the ratio of $1\frac{1}{2}$ to $2\frac{1}{2}$; and should one equivalent of iron combine with one of oxygen, and another compound be formed of two equivalents of iron to three of oxygen, then the oxygen united with the same weight of iron would have the ratio, as in the table, of 1 to $1\frac{1}{2}$. The compounds of manganese and phosphorus with oxygen afford examples of the same nature. Still more complex arrangements will be readily conceived, such as 3 equivalents of one substance to 4, 5, or more of another. But it is remarkable that combinations of this kind are very rare; and even their existence, though theoretically possible, has not been decidedly established. Even some of the compounds which are usually included in the second series belong properly to the first. The red oxide of lead, for instance, appears in its chemical relations not so much as a direct compound of lead and oxygen, but as a kind of salt formed by the union of the binoxide of lead with the protoxide of the same metal. On this supposition the two other oxides belong to the first series.

The merit of establishing the first law of combination seems due to Wenzel, a Saxon chemist; and the second law is deducible from his experiments on the composition of the salts. His work, entitled *Lehre der Verwandtschaft*, was published in 1777. Bergmann and Richter, a few years after, confirmed the observations of Wenzel, though without adding materially in the way of generalization. Higgins in 1789 speculated on the atomic constitution of compound bodies in a manner which, if pursued, would have led to the discovery of Dalton. It is to the latter, science is indebted for deducing from the scattered facts which had been previously collected, a theory of chemical union, embracing the whole science, and giving it a consistency and form which before his time it had never possessed. In his hands the second law of combination first attained its full generality; but the discovery, which is more peculiarly his own, is that part of the third law of combination which is contained in the first of the two series above mentioned. The first public announcement of his views appears to have been made to the Philosophical Society of Manchester in 1803; and in 1808 they were explained in his New System of Chemical Philosophy. In the same year Wollaston and Thomson gave their evidence in support of the new doctrine, and other chemists have followed in the same path of inquiry. But of all who have successfully laboured in establishing the laws of combination, the most splendid contribution is that of the celebrated Berzelius. Struck with the perusal of the works of Richter, he commenced in 1807 an investigation into the Laws of Definite Proportion. Since that period his labours in this important field have been incessant, and every department of the science has been enriched by his skill and indefatigable industry. Whether we look to pneumatic chemistry, to the chemical history of the metals and of the salts, or to the composition of minerals, we are alike indebted to Berzelius. In all has he traced the laws of definite proportion, and by a multitude of exact analyses given to the laws of combination that certainty which accumulated facts can alone convey.

The utility of being acquainted with these important laws is manifest. Through their aid, and by remembering the equivalents of a few elementary substances, the composition of an extensive range of compound bodies may be calculated with facility. Thus by knowing that 6 is the eq. of carbon and 8 of oxygen, it is easy to recollect the composition of carbonic oxide and carbonic acid; the first consisting of 6 parts of carbon + 8 of oxygen, and the second of 6 carbon + 16 of oxygen. The eq. of potassium is 39; and potassa, its protoxide, is composed of 39 of potassium + 8 of oxygen. From these few data, the composition of carbonate and bi-carbonate of potassa are given; the former being composed of 22 parts of carbonic acid + 47 potassa, and the latter of 44 carbonic acid + 47 potassa. This method acts as an artificial memory, the advantage of which, compared with the former practice of stating the composition in 100 parts, will be manifest by inspecting the following quantities, and attempting to recollect them.

	Carbonic Oxide.	Carbonic Acid.
Carbon	42·86	27·27
Oxygen	57·14	72·73

	Carbonate of Potassa.	Bi-carbonate of Potassa.
Carbonic acid	31·43	47·83
Potassa	68·57	52·17

From the same data, calculations, which would otherwise be difficult or tedious, may be made rapidly and with ease, without reference to books, and frequently by a simple mental process. The exact quantities of substances required to produce a given effect may be determined with certainty, thus affording information which is often necessary to the success of chemical processes, and of great consequence both in the practice of the chemical arts, and in the operations of pharmacy.

The same knowledge affords a good test to the analyst by which he may judge of the accuracy of his result, and even sometimes correct an analysis which he has not the means of performing with rigid precision. Thus a powerful argument for the accuracy of an analysis is derived from the correspondence of its result with the laws of chemical union. On the contrary, if it form an exception to them, we are authorized to regard it as doubtful; and may hence be led to detect an error, the existence of which might not otherwise have been suspected. If an oxidized body be found to contain one equivalent of the combustible with 7·99 of oxygen, it is fair to infer that 8, or one equivalent of oxygen, would have been the result, had the analysis been perfect.

The composition of a substance may sometimes be determined by a calculation, founded on the laws of chemical union, before an analysis of it has been accomplished. When the new alkali lithia was first discovered, chemists did not possess it in sufficient quantity for determining its constitution analytically. But the neutral sulphates of the alkalies and alkaline earths are known to be composed of one equivalent of each constituent, and the oxides to contain one eq. of oxygen. If it be found, therefore, by analysis, that neutral sulphate of lithia is composed of 40 parts of sulphuric acid and 14 of lithia, it may be inferred, since 40 is one eq. of the acid, that 14 is the eq. for lithia; and that this oxide is formed of 8 parts of oxygen and 6 of lithium.

The method of determining equivalent numbers will be anticipated from what has already been said. The commencement is made by carefully analyzing a definite compound of two simple substances which possess an extensive range of affinity. Thus water, a compound of oxygen and hydrogen, is found to contain 8 parts of the former to 1 of the latter; and if it be assumed that water consists of 1 eq. of oxygen and 1 of hydrogen, the relative weights of these equivalents will be as 8 to 1. The chemist then selects for analysis such compounds as he believes to contain 1 eq. of each element, in which either oxygen or hydrogen, but not both, is present. Carbonic oxide and hydro-sulphuric acid are suited to his purpose: as the former consists of 8 parts of oxygen and 6 of carbon, and the latter of 1 part of hydrogen and 16 of sulphur, the equivalent of carbon is inferred to be 6, and that of sulphur 16. The equivalent of all the other elements may be determined in a similar manner.

In researches on chemical equivalents there are two kinds of difficulty, one involved in the processes for ascertaining the exact composition of compounds, and the other in the selection of the compounds which contain single equivalents. Important general precautions in the experimental part of the subject are the following:—1, to exert scrupulous care about the purity of materials; 2, to select methods which consist of a few simple operations only; 3, to repeat experiments, and with materials prepared at different times; 4, to arrive at the same conclusion by two or more processes independent of each other. In the selection of compounds of single equivalents there are several circumstances calculated to direct the judgment:—

1. If two substances combine in several proportions, the law of multiples usually effects the electro-negative element of a compound. Thus, in the 5 compounds of nitrogen and oxygen, in which oxygen is the − element, 14 parts of nitrogen are united with 8, 16, 24, 32, and 40 parts of oxygen; whereas, taking the quantity of oxygen as constant, 8 parts of oxygen are united with 14, 7, 4·66, 3·5, and 2·8 parts of nitrogen, in which the simple ratio of the first series does not exist. This circumstance induces the chemist always to search among the oxides of the same element for the lowest grade of oxidation, and in most cases to consider it as a compound of single equivalent. In some instances, however, the second degree of oxidation is formed of single equivalents, while the lowest oxide consists of 2 eq. of the + element and one of oxygen. Such compounds are called *dioxides* (page 137) and sometimes *suboxides.*

2. Metallic oxides, distinguished for strong alkalinity, or for acting as strong alkaline bases, are always protoxides. Dioxides rarely unite definitely with acids, and are remarkable for their ready conversion into protoxides with separation of metal. If the same metal yield several oxides, the protoxide is the strongest base; the highest grade of oxidation is frequently an acid, and the intermediate oxides are in general little distinguished either for alkalinity or acidity. Protoxides usually resist decomposition more obstinately than other oxides.

3. When a metal forms two oxides, the oxygen of which is in the ratio of 1 to $1\frac{1}{2}$, the first is usually the protoxide, and the second a compound of 2 eq. of the metal to three of oxygen. The oxides of iron and nickel are examples.

4. If two compounds resemble each other in their modes of combination, it is a strong presumption that their constitution is

similar. Alumina and the peroxide of iron are remarkably allied in their chemical relations; and hence it is inferred, since the latter consists of 2 eq. of iron and 3 eq. of oxygen, that the former, whose composition would otherwise be very doubtful, is composed of 2 eq. of aluminium and 3 eq. of oxygen.

5. Mitscherlich has found, as is more fully stated in the article on crystallization, that certain compounds which resemble each other in composition and in their modes of combining, are likewise disposed in crystallizing to affect the same form. Hence it is a strong presumption that compounds which are analogous both in their crystalline figure and modes of combining, are also similar in their composition. In the oxide and acid of chromium the oxygen is in the ratio 1 to 2, and hence it was at first supposed that 1 eq. of chromium was united in the oxide with 1 eq. and in the acid with 2. eq. of oxygen. But the chromates resemble the sulphates in form and modes of combining, and the oxide of chromium bears the same analogy to alumina and peroxide of iron. The inference is, that oxide of chromium consists of 2 eq. of chromium and 3 eq. of oxygen, and chromic acid of 1 eq. of chromium and 3 eq. of oxygen.

6. Another guide in these inquiries is derived from the relation traced by Dulong and Petit between the equivalents of a body and its sp. heat. The coincidences pointed out at page 38 are sufficiently numerous to show an interesting relation which is sometimes useful in selecting between doubtful numbers; but the instances of failure are at present too frequent to admit of this principle being used except with much caution.

7. The ready decomposition by galvanism, observed by Faraday, of compounds which consist of single equivalents, and the resistance to the same agent of many others not so constituted, promises to become an indication of great value in determining eq. numbers. The facts as yet known respecting it will be found in the section on galvanism.

8. Great light is often thrown on the chemical constitution of a compound by a knowledge of the *volumes* of the substances of which it is composed. This subject, however, will be discussed in an after part of this section.

Since the equivalents merely express the relative quantities of different substances which combine together, it is in itself immaterial what figures are employed to express them. The only essential point is, that the relation should be strictly observed. Thus, the eq. of hydrogen may be assumed as 10; but then oxygen must be 80, carbon 60, and sulphur 160. We may call hydrogen 100 or 1000; or, if it were desirable to perplex the subject as much as possible, some high uneven number might be selected, provided the due relation between the different numbers were faithfully preserved. But such a practice would destroy the advantage above ascribed to the use of equivalents; and it is the object of every one to employ such as are simple, that their relation may be perceived by mere inspection. Thomson makes oxygen 1, so that hydrogen is eight times less than unity, or 0·125, carbon 0·75, and sulphur 2. Wollaston, in his scale of chemical equivalents, estimated oxygen at 10; and hence hydrogen is 1·25, carbon 7·5, and so on. According to Berzelius, oxygen is 100. And lastly, several other chemists, such as Dalton, Davy, Henry, and others, selected hydrogen as their unit; and therefore the eq. of oxygen is 8. One of these series may easily be reduced to either of the others by an obvious and simple calculation. The numbers adopted in this work refer to hydrogen as unity, and are given in a table (Appendix in Table I.) constructed principally from the published tables of Berzelius, and partly from facts supplied by my own researches. The hypothesis that all equivalent numbers are simple multiples of the eq. of hydrogen, has been elsewhere shown to be untenable. (Phil. Trans. 1833, Part ii. page 523.) Whenever the experimental quantity is nearly a whole number, the last may for many purposes be used as a sufficient approximation; and, accordingly, for such elements as carbon, sulphur, nitrogen, and potassium, which are often referred to in the way of illustration, I have generally adopted round numbers, as being shorter and more easily remembered than fractions. But on all occasions where exact calculations are concerned, the numbers given in the table should be employed.

The useful instrument known by the name of the *Scale of Chemical Equivalents*, was devised by Wollaston, and is a table of equivalents comprehending all those substances which are most frequently employed by chemists in the laboratory; and it only differs from other tabular arrangements of the same kind, in the numbers being attached to a sliding rule, which is divided according to the principle of that of Gunter. From the mathematical construction of the scale, it not only serves the same purpose as other tables of equivalents, but in many instances supersedes the necessity of calculation. Thus, by inspecting the common table of equivalents we learn that 87 parts, or 1 eq. of sulphate of potassa contain 40 parts of sulphuric acid and 47 of potassa: but recourse must be had to calculation, when it is wished to determine the quantity of acid or alkali in any other quantity of the salt. This knowledge, on the contrary, is obtained directly by means of the scale of chemical equivalents. For example, on pushing up the slide until 100 marked upon it is in a line with the name sulphate of potassa on the fixed part of the scale, the numbers opposite to the terms sulphuric acid and potassa will give the precise quantity of each contained in 100 parts of the compound. In the original scale of Wollaston, for a particular account of which I may refer to the Philosophical Transactions for 1814, oxygen is taken as the standard of comparison; but hydrogen may be selected for that purpose with equal propriety, and scales of this kind have been prepared for sale by Reid of Edinburgh. A very complete scale of equivalents has been drawn up by Prideaux of Plymouth. (Phil. Mag. and Annals, viii. 430.)

ON THE ATOMIC THEORY.

The brief sketch which has been given of the laws of combination will, I trust, set in its true light the importance of that department of chemical science. It is founded on experiment alone, and the laws which have been stated are the mere expression of fact. It is not necessarily connected with any speculation, and may be kept wholly free from it. The notion that the laws of combination involve something uncertain or hypothetical, is a fallacy easily referable to its source. It was impossible to reflect on the regularity and constancy with which bodies obey these laws, without speculating about the cause of that regularity; and, consequently, the facts themselves were no sooner noticed, than an attempt was made to explain them. Accordingly, when Dalton published his discovery of those laws, he at once incorporated the description of them with his notion of their physical cause, and even expressed the former in language suggested by the latter. Since that period, though several British chemists of eminence, and in particular Wollaston and Davy, recommended and practised an opposite course, both subjects have been too commonly comprised under the name of *atomic theory;* hence it has often happened that beginners have rejected the whole as hypothetical, because they could not satisfactorily distinguish those parts which are founded on fact from those which are conjectural. All such perplexity would have been avoided, and this department of the science have been far better understood, and its value more justly appreciated, had the discussion concerning the atomic constitution of bodies been always kept distinct from that of the phenomena which it is intended to explain. When employed in this limited sense, the atomic theory may be discussed in a few words.

Two opposite opinions have long existed concerning the ultimate elements of matter. It is supposed, according to one party, that every particle of matter, however small, may be divided into smaller portions, provided our instruments and organs were adapted to the operation. Their opponents contend, on the other hand, that matter is composed of certain ultimate particles or molecules, which by their nature are indivisible, and are hence termed *atoms* (from *α not*, and *τεμνειν to cut*). These opposite opinions have from time to time been keenly contested, and with variable success, according to the acuteness and ingenuity of their respective champions. But it was at last perceived that no positive data existed capable of deciding the question, and its interest therefore gradually declined. The progress of modern chemistry has revived attention to this controversy, by affording a far stronger argument in favour of the atomic constitution of matter than was ever advanced before, and one which is almost irresistible. For the assumption that all bodies consist of ultimate atoms, the weight of which differs in different kinds of matter, supplies a luminous explanation of the laws of chemical union, which do not appear explicable on any other supposition.

According to the atomic theory, every compound is formed of the atoms of its constituents. An atom of A may unite with 1, 2, 3, or more atoms of B. Thus, supposing water to be composed of 1 atom of hydrogen and 1 atom of oxygen, binoxide of hydrogen will consist of 1 atom of hydrogen and 2 atoms of oxygen. If carbonic oxide is formed of 1 atom of carbon and 1 atom of oxygen, carbonic acid will consist of 1 atom of carbon and 2 atoms of oxygen. If, in the compounds of nitrogen and oxygen, enumerated at page 160, the first or protoxide consist of 1 atom of nitrogen and 1 atom of oxygen, the four others will be regarded as compounds of 1 atom of nitrogen to 2, 3, 4, and 5 atoms of oxygen. From these instances it will appear that the law of multiple proportion is a necessary consequence of the atomic theory. There is also no apparent reason why 2 or more atoms of 1 substance may not combine with 2, 3, 4, 5, or more atoms of another; but, on the contrary, these arrangements are necessary in explanation of the not unfrequent occurrence of half equivalents, as formerly stated.

(Page 160.) Such combinations will also account for the complicated proportion noticed in certain compounds, especially in many of those belonging to the animal and vegetable kingdoms.

In consequence of the satisfactory explanation which the laws of chemical union receive by means of the atomic theory, it has become customary to employ the term *atom* in the same sense as combining proportion or equivalent. For example, instead of describing water as a compound of 1 eq. of oxygen and 1 eq. of hydrogen, it is said to consist of 1 atom of each element. In like manner sulphate of potassa is said to be formed of 1 atom of sulphuric acid and 1 atom of potassa, the word in this case denoting as it were a compound atom, that is, the smallest integral particle of the acid or alkali; a particle which does not admit of being divided, except by the separation of its elementary or constituent atoms. The numbers expressing the proportions in which bodies unite must likewise indicate, consistently with this view, the relative weights of atoms; and accordingly these numbers are often called *atomic weights*. Thus, as water is composed of 8 parts of oxygen and 1 of hydrogen, it follows, on the supposition of water consisting of 1 atom of each element, that an atom of oxygen must be 8 times heavier than an atom of hydrogen. If carbonic oxide be formed of an atom of carbon and an atom of oxygen, the relative weights of their atoms are as 6 to 8; and in short the chemical equivalents of all bodies may be considered as expressing the relative weights of their atoms.

The foregoing argument in favour of the atomic constitution of matter becomes much stronger when we trace the intimate connection which subsists among many substances, between their crystalline form and chemical composition. This subject, however, now known under the name of *isomorphism*, will be more conveniently discussed under the head of crystallization.

Dalton supposes the atoms of bodies to be spherical; and he has invented certain symbols to represent the mode in which he conceives they may combine together, as illustrated by the following figures:—

⊙ Hydrogen. ○ Oxygen.
⦶ Nitrogen. ● Carbon.

BINARY COMPOUNDS.

○⊙ Water.
○● Carbonic oxide.

TERNARY COMPOUNDS.

○⊙○ Binoxide of hydrogen.
⊙●○ Carbonic acid.
&c. &c. &c.

All substances containing only 2 atoms he called binary compounds, those composed of 3 atoms ternary compounds, of 4 quaternary, and so on.

There are several questions relative to the nature of atoms, most of which will perhaps never be decided. Of this nature are the questions which relate to the actual form, size, and weight of atoms, and to the circumstances in which they mutually differ. All that we know with any certainty is, that their weights do differ, and by exact analysis the relations between them may be determined. Peculiar views of the constitution of matter are held by Ampère, whose opinions are always acute and philosophical. He not only believes dissimilar atoms, as of oxygen and hydrogen, to be capable of uniting, but that 2 or more atoms of the same kind have a power of mutual attraction whereby they are arranged in groups of definite figure, which he calls *molecules*. These molecules, more or less intimately bound together by cohesion, give rise to the different states of bodies, the sold, liquid, and gaseous. Thus, oxygen gas is conceived not an assemblage of self-repulsive atoms of oxygen, but of molecules, each of which is a polyhedral solid made up of a constant number of atoms and repulsive to neighbouring molecules. In like manner he conceives the ultimate particles of compounds, as water and potassa, to be arranged in groups so as to constitute molecules. Similar views are maintained by Prout in his Bridgewater Treatise. This doctrine receives strong support from some phenomena of gaseous combination, and from the complex nature of organic compounds.

It is but justice to the memory of Higgins, to state that he first made use of the atomic hypothesis in chemical reasonings. In his "Comparative View of the Phlogistic and Antiphlogistic Theories," published in the year 1789, he observes (pages 36 and 37) that "in volatile vitriolic acid a single ultimate particle of sulphur is intimately united only to a single particle of dephlogisticated air; and that, in perfect vitriolic acid, every single particle of sulphur is united to 2 of dephlogisticated air, being the quantity necessary to saturation;" and he reasons in the same way concerning the constitution of water and the compounds of nitrogen and oxygen. These remarks of Higgins do not appear to have had the slightest connection with the subsequent views of Dalton, who seems to have never seen the work of Higgins till after he had given an account of his own doctrine. The observations of Higgins, though highly creditable to his sagacity, do not affect Dalton's merit as an original observer. They were made, moreover, in so casual a manner, as not only not to have attracted the notice of his contemporaries, but to prove that Higgins himself attached no particular interest to them. Dalton's chief merit consists in having formed a complete theory of chemical union, and in the discovery of an essential and most important part of the doctrine, a merit which is solely and indisputably his; but in which he would have been anticipated by Higgins, had that chemist perceived the importance of his own opinions.

To the student who may desire a more ample account of the doctrine of atoms than the nature and limits of this volume admit of being given here, I may recommend a small work by Daubeny on the atomic theory, which in other respects will be found well worthy of persual.

ON THE THEORY OF VOLUMES.

Soon after the publication of the New System of Chemical Philosophy in 1808, in which work Dalton explained his views of the atomic constitution of bodies, Gay-Lussac published in the *Memoires d'Arcueil* on the "Combination of Gaseous Substances with one another." He there proved that gases unite together by volume in very simple proportions, which he exemplified by the ratios in which the following gases unite:—

100	Hydrogen	to	50	Oxygen.
100	Ammoniacal		100	Hydrochloric acid gas.
100	do.		100	Fluoboric acid gas.
100	do.		200	do.
100	do.		100	Carbonic acid gas.
100	do.		200	do.

Various other examples were quoted, both from his own experiments and from those of others, all demonstrating the same fact. Thus ammonia was found by A. Berthollet to consist of 100 volumes of nitrogen gas and 300 volumes of hydrogen; sulphuric acid contains 100 volumes of sulphurous acid and 50 volumes of oxygen; and carbonic acid is formed by burning a mixture of 50 volumes of oxygen and 100 volumes of carbonic oxide.

From these and other instances Gay-Lussac established the fact, that gaseous substances unite in the simple ratio of 1 to 1, 1 to 2, 1 to 3, &c,; and this original observation has been confirmed by such a multiplicity of experiments, that it may be regarded as one of the best established laws in chemistry. Nor does it apply to gases merely, but to vapours also. For example, hydrosulphuric, sulphurous, and hydriodic acid gases are composed of

600 vol.	hydrogen gas and	100 vol.	vapour of	sulphur.
600	oxygen	100	. .	sulphur.
100	hydrogen	100	. .	iodine.

Another remarkable fact established by Gay-Lussac in the same essay is, that the volumes of compound gases and vapours always bear a very simple ratio to the volumes of their elements. This will appear from the following table, in which all the substances are supposed to be in the gaseous taste:—

Volumes of Elements.				Volumes of resulting compounds.
100 Nitrogen	+	300 Hydrogen	yield	200 Ammonia.
50 Oxygen	+	100 Hydrogen	. . .	100 Water.
50 Oxygen	+	100 Nitrogen	. . .	100 Protoxide of Nitrogen.
100 Sulphur	+	600 Hydrogen	. . .	600 Hydrosulphuric acid.
100 Sulphur	+	600 Oxygen	. . .	600 Sulphurous acid.
100 Chlorine	+	100 Hydrogen	. . .	200 Hydrochloric acid.
100 Iodine	+	100 Hydrogen	. . .	200 Hydriodic acid.
100 Bromine	+	100 Hydrogen	. . .	200 Hydrobromic acid.
100 Cyanogen	+	100 Hydrogen	. . .	200 Hydrocyanic acid.
100 Oxygen	+	100 Nitrogen	. . .	200 Binoxide of Nitrogen.

The law of multiples (page 160) is equally demonstrable by means of combining or eq. volumes as by combining or eq. weights. The annexed tabular view will justify this statement:—

Volumes of Elements.				Resulting Compounds.
100 Nitrogen	+	50 Oxygen	yield	Protoxide of Nitrogen.
100 do.	+	100 do.	. . .	Binoxide of Nitrogen.
100 do.	+	150 do.	. . .	Hyponitrous acid.
100 do.	+	200 do.	. . .	Nitrous acid.
100 do.	+	250 do.	. . .	Nitric acid.
100 Hydrogen	+	50 do.	. . .	Water.
100 do.	+	100 do.	. . .	Binoxide of Hydrogen.
100 Carbon Vapour	+	50 do.	. . .	Carbonic oxide.
100 do.	+	100 do.	. . .	Carbonic acid.

It thus appears that the laws of combination may equally well be deduced from the volumes as from the weights of the combining substances, and that the composition of gaseous bodies may be expressed as well by measure as weight. In the subjoined table is a comparative view of equivalent weights and volumes, to which is added the respective sp. gravities in relation both to air and hydrogen: the facts respecting the vapours are drawn from an essay by Mitscherlich. (An. de Ch. et Ph. lv. 5.) In constructing the table 100 volumes of hydrogen are assumed as the unit to which the eq. vol. of other substances are compared, and as the volume occupied by a weight of hydrogen represented by its equivalent. The eq. vol. of other substances, considered as gases, are in like manner the volumes corresponding to their equivalents taken as weights. In all substances, whose sp. gr. and equivalents are the same compared to the sp. gr. and eq. of hydrogen as unity, the eq. vol. is 100. If the sp. gr. is smaller than its equivalent, as in mercury, this must arise from its eq. vol. being proportionally greater than the eq. vol. of hydrogen; and if the sp. gr. is greater than its equivalent, as in oxygen or sulphur, the eq. vol. is proportionally smaller than the eq. vol. of hydrogen. A simple rule of three, therefore, enables the eq. vol. to be calculated. Thus the eq. vol. of mercury is $\frac{202}{101} \times 100 = 200$; that of oxygen $\frac{8}{16} \times 100 = 50$; and that of sulphur is $\frac{16{\cdot}10}{96{\cdot}48} \times 100 = 16{\cdot}66$, agreeably to the numbers which will be found in the table.

Gas and Vapours.	Specific Gravities.		Chemical Equivalents.	
	Air as 1.	Hydrogen as 1.	By Vol.	By Weight.
Hydrogen	0·0690	1·00	100	1·00
Nitrogen	0·9727	14·12	100	14·15
Chlorine	2·4700	35·84	100	35·42
Carbon (hypothetical)	0 4215	6·12	100	6·12
Iodine	8·7011	126·30	100	126·30
Bromine	5·3930	78·40	100	78·40
Water	0·6202	9·00	100	9·00
Alcohol	1·6012	23·24	100	23·25
Sulphuric Ether	2·5822	37·50	100	37·50
Light Carburetted Hydrogen	0·5595	8·12	100	8·12
Olefiant Gas	0·9810	14·24	100	14·24
Carbonic Oxide	0·9727	14·12	100	14·12
Carbonic Acid	1·5239	22·12	100	22·12
Protoxide of Nitrogen	1·5239	22·12	100	22·15
Sulphurous Acid	2·2105	32·10	100	32·10
Sulphuric Acid (anhydrous)	2·7617	40·10	100	40·10
Cyanogen	1·8157	26·35	100	26·35
Hydrosulphuric Acid	1·1770	17·10	100	17·10
Binoxide of Nitrogen	1·0377	15·06	200	30·15
Mercury	6·9690	101·00	200	202·00
Ammonia	0·5898	8·56	200	17·15
Hydrochloric Acid	1·2695	18·42	200	36·42
Hydriodic Acid	4·3850	63·63	200	127·26
Hydrobromic Acid	2·7310	39·71	200	79·40
Hydrocyanic Acid	0·9423	13·67	200	27·35
Arsenuretted Hydrogen	2·6950	39·20	200	78·20

Gas and Vapours.	Specific Gravities.		Chemical Equivalents.	
	Air as 1.	Hydrogen as 1.	By Vol.	By Weight.
Sesquichloride of Arsenic	6·2950	91·36	200	181·66
Sesquiodide of Arsenic	15·6400	227·00	200	454·28
Protochloride of Mercury	8·2040	119·00	200	237·42
Bichloride of Mercury	9·4390	137·00	200	272·84
Bromide of Mercury	9·6650	140·26	200	280·40
Bibromide of Mercury	12·3620	179·40	200	358·80
Biniodide of Mercury	15·6700	227·40	200	454·52
Oxygen	1·1025	16·00	50	8·00
Arsenious Acid	13·6695	198·4	50	99·40
Phosphorus	4·3273	62·8	25	15·70
Arsenic	10·3620	150·8	25	37·7
Sulphur	6·6480	96·48	16·66	16·10
Bisulphuret of Mercury	5·3840	78·10	33·33	234·18

The observations which more immediately flow from the facts in the preceding table are these:—

1. The combining or eq. volumes of substances, both elementary and compound, are either equal or have the simple ratio of 1 to 1, 1 to 2, 1 to 3, &c. The same simplicity rarely exists among the equivalent weights.

2. On comparing together the third and fifth columns, the corresponding numbers for the 18 first substances will be found nearly or quite identical. As those substances have the same uniting volume as hydrogen, which is the assumed unit of comparison, and as the sp. gravities are merely the weights of equal volumes, the numbers of the third column, were they quite exact, must coincide with those in the fifth: their want of identity indicates errors of observation.

3. The identity in the eq. volumes of the elementary gases, hydrogen, nitrogen, and chlorine, led to the notion that the eq. volumes of most other elements, such as carbon, sulphur, and phosphorus, might also be identical. *Assuming* that identity, the sp. gravity which those elements ought to have when gaseous, may easily be calculated. Thus, taking 1, 6·12, and 16·1 as the equivalents of hydrogen, carbon, and sulphur, then will their sp. gravities in the gaseous state, eq. volumes being supposed equal, be in the ratio of 1, 6·12, and 16·1. This method, by which the hypothetical sp. gravity of carbon, as stated in the table, was obtained, was first indicated by Dr. Prout. (An. of Phil. vi. 321.) But though such hypothetical numbers may sometimes be used for the convenience of expressing the relation of uniting substances by measure, recent

facts show how dangerous it would be to confide in them; for by the table it appears that the eq. volume of sulphurous vapour is one sixth of that of hydrogen, which renders the sp. gravity of the vapour of sulphur six times greater than the hypothetical number. Similar deviation is observable in phosphorus, arsenic, and mercury. In these cases, the real sp. gravity of a vapour is as much greater or less than the hypothetical as its eq. volume is less or greater than that of hydrogen.

4. The identity in the eq. volumes of hydrogen, nitrogen, and chlorine, suggested the idea that the atoms of all the elements are of the same magnitude; and this, coupled with the supposition that the self-repulsive energy of these atoms is equal, led to the opinion that equal volumes of the elements in the gaseous state must contain an equal number of atoms. This hypothesis, recommended by its simplicity, and supported by the fact that the volumes of gaseous substances vary according to the same law by varying temperature and pressure, was accordingly employed as a mode of determining the relative weights of atoms. As water consists of 50 measures of oxygen and 100 of hydrogen gas, it was inferred to be a compound of one atom of oxygen and two atoms of hydrogen; and consequently, taking 8 as the weight of an atom of oxygen, the weight of one atom of hydrogen is $\frac{1}{2}$ instead of 1, as in the table; or taking hydrogen as 1, the atom of oxygen is 16. On the same principle may the numbers which in the table represent the eq. weights of chlorine, bromine, iodine, and nitrogen, which have the same eq. volumes as hydrogen, be considered as the weights of two equivalents. The equivalents adopted by Davy in his Elements of Chemical Philosophy, as well as those of Berzelius, which are now in general use on the Continent, were framed in accordance with these views: this the British chemist requires to bear in mind, since the same numbers which Berzelius uses for 2 eq. of hydrogen, nitrogen, chlorine, bromine, and iodine, he considers as one equivalent. But the opinion of Davy and Berzelius must now either be abandoned, or maintained on other principles, since the late researches of Dumas and Mitscherlich have shown experimentally that eq. volumes of the elementary gases and vapours do not contain the same number of atoms.

5. The facts contained in the last and preceding tables supply material for calculating the sp. gravity of compound gases, by which means the accuracy of other conclusions respecting their composition may be verified. This analysis proves that ammoniacal gas is com-

posed of 100 volumes of nitrogen and 300 of hydrogen gases, condensed into the space of 200 volumes: if so, its sp. gravity will be

$$\frac{0{\cdot}9727+3\times0{\cdot}069}{2}=\frac{1{\cdot}1797}{2}=0{\cdot}5889.$$

The near agreement of this calculated number with that found by weighing the gas itself, proves that ammonia has really the constitution above assigned to it, and gives great probability that the sp. gravity of nitrogen and hydrogen gases is nearly correct.

Again, hydrochloric acid gas consists of 100 volumes of hydrogen and 100 of chlorine gases united without any change of bulk. Hence its sp. gravity ought to be

$$\frac{2{\cdot}47+0{\cdot}069}{2}=1{\cdot}2695.$$

Hydrocyanic acid vapour is formed of 100 volumes of hydrogen and 100 of cyanogen gases united without change of volume; and therefore its sp. gravity should be

$$\frac{1{\cdot}8157+0{\cdot}069}{2}=0{\cdot}9423.$$

Considering olefiant gas as a compound of 200 volumes of hydrogen gas and 200 of the vapour of carbon condensed into 100, its sp. gravity will be $2\times0{\cdot}069+2\times0{\cdot}4215=0{\cdot}1380+0{\cdot}8430=0{\cdot}9810$.

Aqueous vapour is composed of 100 volumes of hydrogen and 50 of oxygen gases condensed into the space of 100 volumes; and therefore its sp. gravity ought to be $0{\cdot}069+0{\cdot}5512$ (half the sp. gr. of oxygen) $=0{\cdot}6202$.

Protoxide of nitrogen is formed of 100 volumes of nitrogen and 50 of oxygen gases condensed into 100 volumes, and hence its sp. gravity should be $0{\cdot}9727+0{\cdot}5512=1{\cdot}5239$.

Assuming carbonic oxide to be a compound of 100 volumes of carbon vapour and 50 of oxygen gas contracted in uniting into 100 volumes, its sp. gravity should be $0{\cdot}4215+0{\cdot}5512=0{\cdot}9727$.

As the different sp. gravities thus calculated are very nearly those found by direct experiment, there is a strong presumption that the elements of the calculations are correct.

The principle of these calculations is sufficiently obvious. The sp. gravities represent the weights of equal volumes of the gases;

taking 100 as the standard volume of which the sp. gravity of each gas denotes the weight, then 50 volumes of a gas may be indicated by half, 25 volumes by a fourth, and 16·66 by a sixth of its sp. gravity. Thus hydrosulphuric acid is a compound of 100 volumes of hydrogen gas, and 16·66 ($\frac{100}{6}$) of the vapour of sulphur condensed into 100 volumes, and therefore its sp. gravity is

$$0{\cdot}069+\frac{6{\cdot}6480}{6}=0{\cdot}069+1{\cdot}1080=1{\cdot}1770.$$

Sulphurous acid consists of 100 volumes of oxygen gas and 16·66 of the vapour of sulphur condensed into 100 volumes; and hence its sp. gravity is

$$1{\cdot}1025+\frac{6{\cdot}6480}{6}=1{\cdot}1025+1{\cdot}1080=2{\cdot}2105.$$

In these two gases the volume is the same as the hydrogen or oxygen which they contain, and therefore their sp. gravities are the sum of the weights of their elements. The same applies to water, protoxide of nitrogen, and carbonic oxide. In olefiant gas 400 volumes are condensed into 100, and therefore its sp. gravity is the sum of the sp. gravities of its elements. Hydrochloric acid gas occupies the same space as its elements, and therefore its sp. gravity is found by taking the mean of their sp. gravities. The same remark applies to hydrocyanic acid. In ammonia 400 volumes are condensed into 200, and therefore the sum of the sp. gravities is halved.

As vapours are easily condensed by cold, and in many cases exist as such only at high temperatures, their sp. gravities may often be obtained by calculation more accurately than by experiment. Thus it is easier accurately to ascertain the sp. gravity of hydrogen and hydrosulphuric acid gases than of the vapour of sulphur; and therefore as soon as experiment has shown that the sp. gravity of that vapour is *somewhere about* 6·6480, then the precise number may be calculated. For as 100 volumes of hydrosulphuric acid gas contain 100 of hydrogen gas, the sp. gravity of the latter deducted from that of the former (1·177 − 0·069), gives 1·108 as the weight of combined sulphur. If the eq. volume of sulphur were 100, then must 1·108 be its sp. gravity; but as the number found experimentally is nearly six times 1·108, the inference is that the real sp. gravity is 6 × 1·108 = 6·648, and that its eq. volume is six times less than 100, or 16·66. The only assumption here is, that if the eq. volume of the vapour is not 100, it must be some multiple or submultiple of it by a whole number, consistently with the *theory of volumes.* In the construction of the preceding table I have given the sp. gravities of vapours calculated on these principles rather than the precise numbers given by experiment.

6. The volume of a compound gas in reference to the volumes of its components is determined by one of the following rules:—

1. One volume of gas united with one volume, yield two volumes of the compound.

2. The volume of the compound gas often has the volume of that gas which enters most largely into it by volume.

3. The volume of the compound gas is equal to the sum of the volumes of its components divided generally by 2, but sometimes by 4 or 8.

4. In a few cases the sum of the component volumes must be divided by 3.

CHEMICAL SYMBOLS.

The impracticability in many cases of contriving convenient names expressive of the constitution of chemical compounds, especially of minerals, suggested the employment of symbols as an abbreviated mode of denoting the composition of bodies. It was thought that the names of elementary substances, instead of being written at full length, might often be more conveniently indicated by the first letter of their names; and that the combination of elements with each other might be expressed by placing together, in some way to be agreed on, the letters which represent them. The advantage of such a symbolic language was felt so strongly by Berzelius, that he some years ago contrived a set of symbols, which he has since used extensively in his writings; and other eminent chemists as well as mineralogists, believing symbols to be useful, adopted those which Berzelius had proposed. The consequence is, that symbolic expressions, called *chemical formulæ,* are now so much resorted to, and are so identified with the language of chemistry, that essays of great value are in a measure as sealed books to those who cannot read symbols. It is therefore important that the chemical student, whatever he may think of the value of symbols, should not be unacquainted with them. Fortunately, the labour of a few minutes will enable him to understand the subject. The following table includes the symbols of all the elementary substances according to Berzelius.

TABLE OF SYMBOLS.

Elements.	Symb.	Elements.	Symb.	Elements.	Symb.
Aluminium	Al	Gold (Aurum)	Au	Potassium (Kalium)	K
Antimony (Stibium)	Sb	Hydrogen	H	Rhodium	R
Arsenic	As	Iodine	I	Selenium	Se
Barium	Ba	Iridium	Ir	Silicon	Si
Bismuth	Bi	Iron (ferrum)	Fe	Silver (Argentum)	Ag
Boron	B	Lead (Plumbum)	Pb	Sodium (Natrium)	Na
Bromine	Br	Lithium	L	Strontium	Sr
Cadmium	Cd	Magnesium	Mg	Sulphur	S
Calcium	Ca	Manganese	Mn	Tellurium	Te
Carbon	C	Mercury (Hydrargyrum)	Hg	Thorium	Th
Cerium	Ce	Molybdenum	Mo	Tin (Stannum)	Sn
Chlorine	Cl	Nickel	Ni	Titanium	Ti
Chromium	Cr	Nitrogen	N	Tungsten (Wolfram)	W
Cobalt	Co	Osmium	Os	Vanadium	V
Columbium (Tantalum)	Ta	Oxygen	O	Uranium	U
Copper (Cuprum)	Cu	Palladium	Pd	Yttrium	Y
Fluorine	F	Phosphorus	P	Zinc	Zn
Glucinium	G	Platinum	Pl	Zirconium	Zr.

For the sake of uniformity, and to prevent confusion, it is much to be wished that these symbols, being now generally known, should be rigorously adhered to. Berzelius has properly selected them from Latin names, as being known to all civilized nations; and when the names of two or more elements begin with the same letter, the distinction is made by means of an additional letter.

The foregoing symbols are intended to represent the chemical eq. of the elements. Thus, the letters H, I, and Ba, stand for 1 eq. of hydrogen, iodine, and barium; and 2 H, 3 H, and 4 H, for 2, 3, and 4 eq. of hydrogen. Two eq. of an element are often denoted by placing a dash through or under its symbol: for instance, $\mathrm{H\!\!\!\!-}$ or $\underline{\mathrm{H}}$ means 2 H, and $\mathrm{P\!\!\!\!-}$ or $\underline{\mathrm{P}}$ signifies 2 P. Certain compounds are often, for the sake of brevity, denoted by single symbols in the same manner as the elements: thus an eq. of water, ammonia, and cyanogen, is sometimes expressed by Aq, Am, and Cy; but in general the formulæ for compound bodies are so contrived as to indicate the elements they contain, and the mode in which they are united. This may be done in several ways; but that which first suggests itself is, to connect together the symbols by the same signs as are used in Algebra. Thus the formulæ $K+O$, $Ca+O$, $Ba+O$, $Mn+O$, $Fe+O$, $2\,Fe+3\,O$, $3\,H+N$, $2\,H+2\,C$, $C+2\,O$, $N+5\,O$, $S+3\,O$, and $H+Cl$, denote single eq. of potassa, lime, baryta, protoxide of manganese, protoxide of iron, peroxide of iron, ammonia, olefiant gas, carbonic acid, nitric acid, sulphuric acid, and hydrochloric acid. The formula $K + N + 6\,O$ indicates the elements which are contained in an eq. of nitrate of potassa: in order to express further that the potassium is combined with only 1 eq. of oxygen, the remaining oxygen with the nitrogen, and the potassa with nitric acid, the symbols are placed thus, $(K + O) + (N + 5\,O)$, the brackets containing the symbols of those elements which are supposed to be united. A number placed on the outside of a bracket multiplies the compound within it: thus $(K + O) + (S + 3\,O)$ is sulphate of potassa, and $(K + O) + 2\,(S + 3\,O)$ is the bisulphate. All the elements contained in a compound are thus visibly represented, and the chemist is able readily to trace all possible modes of combination, and to select that which is most in harmony with the facts and principles of his science. He may, and often does, thereby detect relations which might otherwise have escaped notice.

Another advantage attributable to such formulæ is, that they facilitate the comprehension of chemical changes. If hydro-sulphuric acid acts upon the protoxide of lead, it is easy to say that the sulphur combines with the lead and the hydrogen with the oxygen; but the exact adaptation of the quantities for mutual interchange appears to me more clearly shown by symbols than by a description or a diagram, both of which are apt to produce confusion where the change to be explained is complex. In the simple instance alluded to, $H + S$ reacts on $Pb + O$, and the products are $Pb + S$ and $H + O$. When hydrosulphuric acid acts on bicyanuret of mercury, the result is bisulphuret of mercury and hydrocyanic acid: the substances which interchange elements are $2\,(H + S)$ and $Hg + 2\,Cy$; and the products are $Hg + 2\,S$, and $2\,(H + Cy)$. In more complicated changes the advantage of chemical formulæ is still more manifest, examples of which kind will be found in the section on cyanogen, and in other parts of this volume.

Useful as the algebraic chemical formulæ are for the purpose of studying chemical changes, they are sometimes found inconveniently long where the object is merely to express the composition of bodies, and accordingly Berzelius has introduced several abbreviations. For instance, he indicates degrees of oxidation by dots placed over the symbol, writing $\dot{K}$, $\ddot{C}$, $\overset{\cdot\cdot\cdot\cdot\cdot}{N}$, instead of $K + O$, $C + 2O$, $N + 5O$, for potassa, carbonic acid, and nitric acid. In like manner he denotes compounds of sulphur by commas, writing $\overset{,}{K}$, $\overset{,,}{Hg}$, $\overset{,}{H}$ instead of $K + S$, $Hg + 2\,S$, $H + S$, for sulphuret of potassium, bisulphuret of mercury, and hydrosulphuric acid. When the ratio is that of 2 to 3 he employs the symbol for two eq. above stated: thus, $\underline{\overset{\cdots}{\mathrm{Fe}}}$, $\underline{\overset{\cdot\therefore\cdot}{\mathrm{P}}}$, $\underline{\overset{\cdot\therefore\cdot}{\mathrm{As}}}$, is used instead of $2\,\mathrm{Fe} + 3\mathrm{O}$, $2\mathrm{P} + 5\mathrm{O}$, $2\mathrm{As} + 5\mathrm{O}$, for an equivalent of peroxide of iron, phosphoric acid, and arsenic acid; and similarly we have $\underline{\overset{,,,}{\mathrm{A}}\mathrm{s}}$, $\underline{\overset{,;,;}{\mathrm{A}}\mathrm{s}}$, instead of $2\,\mathrm{As} + 3\,\mathrm{S}$, $2\,\mathrm{As} + 5\,\mathrm{S}$ for the sesquisulphuret and persulphuret of arsenic. These last formulæ are sometimes used to indicate two eq. instead of one; but as, agreeably to the atomic theory, the smallest possible particle of peroxide of iron consists of 2 atoms of iron and 3 of oxygen, the formula $2\,\mathrm{Fe} + 3\,\mathrm{O}$ ought to stand for 1 eq. only.

Berzelius often dispenses with the sign, +, and writes combined elements side by side, the sign of addition being understood instead of expressed. Thus he uses HO, KO, FeS, $\dot{\mathrm{C}}\mathrm{a}\,\ddot{\mathrm{C}}$, $\dot{\mathrm{B}}\mathrm{a}\,\overset{\cdot\therefore\cdot}{\mathrm{N}}$, $\dot{\mathrm{K}}\,\dddot{\mathrm{S}} + \dot{\mathrm{N}}\mathrm{i}\,\dddot{\mathrm{S}}$, instead of $\mathrm{H} + \mathrm{O}$, $\mathrm{K} + \mathrm{O}$, $\mathrm{Fe} + \mathrm{S}$, $\dot{\mathrm{C}}\mathrm{a} + \ddot{\mathrm{C}}$, $\dot{\mathrm{B}}\mathrm{a} + \overset{\cdot\therefore\cdot}{\mathrm{N}}$, $(\dot{\mathrm{K}} + \dddot{\mathrm{S}},) + (\dot{\mathrm{N}}\mathrm{i} + \dddot{\mathrm{S}})$, for water, potassa, sulphuret of iron, carbonate of lime, nitrate of baryta, and the double sulphate of potassa and oxide of nickel. Two or more equivalents of one constituent of a compound are denoted by numbers placed in the same position as the indices of powers in algebra: thus NH^3, NC^2, $\underline{\overset{\cdots}{\mathrm{Fe}}}^2$, H^3, is the abbreviation of $\mathrm{N} + 3\mathrm{H}$, $\mathrm{N} + 2\mathrm{C}$, $2\underline{\overset{\cdots}{\mathrm{Fe}}}, + 3\dot{\mathrm{H}}$ for ammonia, cyanogen, and sesquihydrate of iron, a compound of 2 eq. of peroxide of iron and 3 of water. A number used before symbols, like coefficients in algebra, multiplies all the following symbols not separated from it by a + sign. Thus in $8\;\dot{\mathrm{C}}\mathrm{a}\;\dddot{\mathrm{S}}\mathrm{i} + \dot{\mathrm{K}}\;\dddot{\mathrm{S}}^2 + 16\ \mathrm{aq.}$ (which is the formula for the mineral called apophyllite) the 8 denotes 8 eq. of $\dot{\mathrm{C}}\mathrm{a}\;\dddot{\mathrm{S}}\mathrm{i}$, or silicate of lime, which are united with 1 eq. of bisilicate of potassa, and 16 of water.

Berzelius also expresses the vegetable and animal acids by the first letter of their name, with a dash over it. Thus $\overline{\mathrm{T}}$, $\overline{\mathrm{A}}$, $\overline{\mathrm{C}}$, $\overline{\mathrm{B}}$, $\overline{\mathrm{G}}$, $\overline{\mathrm{F}}$, are the symbols for tartaric, acetic, citric, benzoic, gallic, and formic acids.

Several objections, some of which are of great weight, have been made to this system of symbols, and various modifications have been proposed by different authors. Among these, that which has been adopted by Liebig and Poggendorff in their chemical dictionary, combine more successfully than any other the requisite clearness, brevity, and generality, and will be used in this work. The following are the principles of this method. The numbers which are written before a symbol affect all that follow as far as the first full stop or sign of addition; while those which are written a little below and to the right hand, multiply only the symbol to which they are attached. Two symbols placed side by side are understood to be combined together; thus HO signifies water; KO potash, &c. When two compounds are separated only by a comma, they are also to be considered as combined. Thus KO,HO is the symbol of hydrate of potash; KO,SO_3 that of sulphate of potash. When two salts or other complex compounds are combined, the + sign is used; thus $KO,SO_3 + HO,SO_3$ represents bisulphate of potash, a compound of sulphate of potash with hydrated sulphuric acid. In this system of notation, no dots are employed, nor is any abbreviation used to express two equivalents. For example, alumina, which Berzelius abbreviates thus, $\overset{\cdots}{\underline{Al}}$, is represented by Al_2O_3, which is equally short, more easily written and printed, and which moreover has this advantage, that there is only one symbol used for each element; while the composition of allied compounds admits of a more ready comparison. If, for example, it is wished to show the analogy between the oxides and chlorides of phosphorus, this is at once done by writing their formulæ according to the method of Liebig and Poggendorff.

$$P_2O_3\ P_2O_5\ P_2Cl_3\ P_2Cl_5$$

Whereas if dots are employed for oxygen, the analogy is far from being so obvious:—

$$\overset{\cdots}{\underline{P}}\ \overset{\cdot\cdot\cdot\cdot\cdot}{\underline{P}}\ \underline{P}Cl^3\ \ \underline{P}Cl^5$$

unless chlorine be like oxygen, expressed in two ways; which, however, would embarrass the learner unnecessarily. By comparing the symbol for apophyllite, according to Berzelius, above given, with that for the same mineral, according to Liebig and Poggendorff, $8(CaO,SiO_3) + KO,2SiO_3 + 16$ aq., it will be seen that the latter is at least equally clear, and from the absence of dots, far less liable to error in printing or in reading. In the first limb of the above formula it is to be observed that the figure 8 multiplies all contained within the parenthesis. In like manner, crystallised alum is represented, according to Berzelius, by $\dot{K}\overset{\cdots}{S} + \overset{\cdots}{\underline{Al}}\,\overset{\cdots}{S}{}^3 + 24\dot{H}$; and, on the method here preferred, by $KO,SO_3 + Al_2O_3,3SO_3 +$

24HO. For the reasons above mentioned, the method of Liebig and Poggendorff will be uniformly employed hereafter; but I have thought it right to explain that of Berzelius, that where it is met with it may be understood.

ISOMERIC BODIES.

It was formerly thought that the same elements united in the same ratio must always give rise to the same compound; but within these few years several examples have been discovered of two or even more substances containing the same elements in the same ratio, and yet exhibiting chemical properties distinct from each other. For such compounds Berzelius has suggested the general appellation of *isomeric*, from *ισος equal*, and *μερος part*, expressive of equality in the ingredients. Interesting instances of this kind are the two cyanic acids, which consist of cyanogen and oxygen in the same ratio, and have the same equivalent, yet differ widely in their chemical properties; and a similar example is afforded by the tartaric and paratartaric acids. Para from *παρα near to*, is prefixed in order to mark the relation to tartaric acid, a principle of nomenclature which is extended to other cases.

Unexpected as was the discovery of isomerism, it is quite consistent with our theories of chemical union, insomuch as the same elements may be grouped or combined in different ways, and thereby give rise to compounds essentially distinct. Thus the elements of sulphate of potassa may perhaps be united indiscriminately with each other, as expressed by the formula KSO_4; or they may form $KO + SO_3$; or $KS + O_4$; or $KO_2 + SO_2$; and other combinations might be made. The second of these is thought to be the real one; but no one can say that the others are impracticable. Again, the elements of peroxide of tin, Sn and 2O, may either form SnO_2, or $SnO + O$; and those of the peroxide of iron, 2Fe and 3O, may either be Fe_2O_3, or $FeO + FeO_2$, not to mention other possible combinations. The elements of alcohol are 4C, 6H, and 2O, which may be united indiscriminately as $H_6C_4O_2$, $H_6C_4 + 2O$, $H_5C_4O + HO$, or $H_4C_4 + 2HO$, besides others.

Some bodies consist of the same elements in the same ratio, and yet differ in their equivalents. A marked example is supplied by olefiant gas and etherine, the former of which contains 200 volumes of carbon vapour and 200 of hydrogen gas condensed into 100 volumes, and the latter of 400 volumes of carbon vapour and

400 of hydrogen gas, united so as to yield 100 volumes of etherine. The equivalent of olefiant gas is 14·24, and that of etherine 28·48, or exactly double. A similar case will be found in the description of cyanuric acid. The nature of these compounds is at once detected by their equivalents being unlike, and by the volume which they occupy as gases compared with the volumes of the elements of which they consist. Isomeric bodies of this kind are obviously much less intimately allied than those above described.

SECTION III.

OXYGEN.

History.—Discovered by Priestley in 1774, and by Scheele a year or two after, without previous knowledge of Priestley's discovery. It was termed *Dephlogisticated air* by Priestley, *Empyreal air* by Scheele, and *Vital air* by Condorcet. The name it now bears, derived from the Greek words οξυς *acid* and γενναειν *to generate*, was proposed by Lavoisier, who considered it the sole cause of acidity.

Preparation.—From several sources, the peroxides of manganese, lead, and mercury, nitre, and chlorate of potassa, yield it in large quantities when they are exposed to a red heat. The substances commonly employed for the purpose are peroxide of manganese and chlorate of potassa. It may be procured from the former in two ways; either by heating it to redness in a gun-barrel, or in a retort of iron or earthenware; or by putting it in fine powder into a flask with about an equal weight of concentrated sulphuric acid, and heating the mixture by means of a lamp. To understand the theory of these processes, it is necessary to bear in mind the composition of the three following oxides of manganese:—

	Manganese.	Oxygen.	
Protoxide	27·7 or 1 equiv.	+ 8	=35·7
Sesquioxide	27·7	+ 12	=39·7
Peroxide	27·7	+ 16	=43·7

On applying a red heat to the last, it parts with half an equivalent of oxygen, and is converted into the sesquioxide. Every 43·7 grains of the peroxide will therefore lose, if quite pure, 4 grains of oxygen, or nearly 12 cubic inches; and one ounce will yield about

128 cubic inches of gas. With sulphuric acid the peroxide loses a whole eq. of oxygen, and is converted into the protoxide, which unites with the acid, forming a sulphate of the protoxide of manganese. Every 43·7 grains of peroxide yields 8 grains of oxygen and 35·7 of protoxide, which by uniting with one eq. (40) of the acid, forms 75·7 of the sulphate. The first of these processes is the most convenient in practice.

The gas obtained from peroxide of manganese, though hardly ever quite pure, owing to the presence of iron, carbonate of lime, and other earthy substances, is sufficiently good for ordinary purposes. It yields a gas of better quality, if previously freed from carbonate of lime by dilute hydrochloric or nitric acid; but when oxygen of great purity is required, it is better to obtain it from chlorate of potassa. For this purpose, the salt should be put into a retort of green glass, or of white glass made without lead, and be heated nearly to redness. It first becomes liquid, though quite free from water, and then, on increase of heat, is wholly resolved into pure oxygen gas, which escapes with effervescence, and into a white compound, called chloride of potassium, which is left in the retort. The composition of the chloric acid and potassa which constitute the salt, is stated below:—

Chlorine .	35·42 or 1 eq.	Potassium .	39·15 or 1 eq.
Oxygen .	40 or 5 eq.	Oxygen .	8 or 1 eq.
Chloric acid .	75·42 or 1 eq.	Potassa .	47·15 or 1 eq.

Hence the oxygen which passes over from the retort, is derived partly from the potassa and partly from the chloric acid; while chlorine and potassium enter into combination. Thus are 122·57 grains of the chlorate resolved into 74·57 grains of chloride of potassium, and 48 grains, or about 161 cubic inches of pure oxygen. The following equation briefly and clearly explains the change, $KO + ClO_5 = KCl + O_6$.

Properties.—Colourless, tasteless, inodorous; feeble refraction of light; non-conductor of electricity; heavier than atmospheric air, sp. gr. being estimated at 1·1026 by Dulong and Berzelius, so that 100 cubic inches weigh at 60° and 30′ Bar. 34·193 grains. It is always gaseous when not combined with other ponderable matter; though even in its simplest form it is associated, like other elementary principles, with the agents productive of heat, light, and electricity. Like all gases it emits a strong heat when suddenly compressed: light also appears; but this is solely due to its chemical action on the oil with which the compressing tube is lubricated. It is the most perfect — electric, always appearing at the + electrode when any of its compounds is electrolized; is sparingly absorbed by water, which dissolves only 3 or 4 per cent. of the gas; is neither acid nor alkaline, as it does not change the colour of blue flowers, nor evince a disposition to unite directly either with acids or alkalies. It has a very powerful attraction for most simple substances; and there is not one of them, except perhaps the highly-negative fluorine, with which it may not be made to combine. The act of combining with oxygen is called *oxidation*, and bodies which have united with it are said to be *oxidized.* The compounds so formed are divided by chemists into acids and oxides. The former division includes those compounds which possess the general properties of acids; and the latter comprehends those which not only do not possess that character, but of which many are highly alkaline, and yield salts by uniting with acids. The phenomena of oxidation are variable. It is sometimes produced with great rapidity, and with evolution of heat and light. Ordinary combustion, for instance, is nothing more than rapid oxidation; and all inflammable or combustible substances derive their power of burning in the open air from their affinity for oxygen. On other occasions it takes place slowly, and without any appearance either of heat or light, as in the rusting of iron by moist air. Different as these processes may appear, oxidation is the result of both; and both depend on the same circumstance, namely, the presence of oxygen in the atmosphere.

All substances that are capable of burning in the open air, burn with far greater brilliancy in oxygen gas. A piece of wood, on which the least spark of light is visible, bursts into flame the moment it is put into a jar of oxygen; lighted charcoal emits beautiful scintillations; and phosphorus burns with so powerful and dazzling a light that the eye cannot bear its impression. Even iron and steel, which are not commonly ranked among the inflammables, undergo rapid combustion in oxygen gas.

The changes that accompany these phenomena are no less remarkable than the phenomena themselves. When a lighted taper is put into a vessel of oxygen gas, it burns for a while with increased splendour; but the size of the flame soon begins to diminish, and if the mouth of the jar be closed, the light will in a short time disappear entirely. The gas has now lost its characteristic property; for a second lighted taper, immersed in it, is instantly extinguished.

This result is general. The burning of one body in a given portion of oxygen unfits it more or less completely for supporting the combustion of another; and the reason is manifest. Combustion is produced by the combination of inflammable matter with oxygen. The quantity of free oxygen, therefore, diminishes during the process, and is at length nearly or quite exhausted. The burning of all bodies, however inflammable, must then cease, because the presence of oxygen is necessary to its continuance. For this reason oxygen gas is called a supporter of combustion. Oxygen often loses its gaseous form as well as its other properties. If phosphorus or iron be burned in a jar of pure oxygen over water or mercury, the disappearance of the gas becomes obvious by the ascent of the liquid, which is forced up by the pressure of the atmosphere, and fills the vessel. Sometimes, on the contrary, the oxygen gas suffers diminution of volume only, or it may even undergo no change of bulk at all, as is exemplified by the combustion of the diamond.

The changes experienced by the burning body are equally striking. While the oxygen loses its power of supporting combustion, the inflammable substance lays aside its combustibility. It is then an oxidized body, and cannot be made to burn even by aid of the purest oxygen gas. It has also increased in weight. It is an error to suppose that bodies lose any thing while they burn. The materials of our fires and candles do indeed disappear, but they are not destroyed. Although they fly off in the gaseous form, and are commonly lost to us, it is not difficult to collect and preserve all the products of combustion. When this is done with the required care, the combustible matter is always found to weigh more after than before combustion; and the increase in weight is exactly equal to the quantity of oxygen which has disappeared during the process.

Oxygen gas is necessary to respiration. No animal can live in an atmosphere which does not contain a certain portion of uncombined oxygen; for an animal soon dies if put into a portion of air from which the oxygen has been previously removed by a burning body. Oxygen disappears during respiration. If a bird be confined in a limited quantity of atmospheric air, it will at first feel no inconvenience; but as a portion of oxygen is withdrawn at each inspiration, its quantity diminishes rapidly, so that respiration soon becomes laborious, and in a short time ceases altogether. Should another bird be then introduced into the same air, it will die in the course of a few seconds; or if a lighted candle be immersed in it, its flame will be extinguished. Respiration and combustion have therefore the same effect. An animal cannot live in an atmosphere which is unable to support combustion; nor, in general, can a candle burn in air which contains too little oxygen for respiration.

It is singular that, though oxygen is necessary to respiration, in a state of purity it is deleterious. When an animal, as a rabbit for example, breathes pure oxygen gas, no inconvenience is at first perceived; but after the interval of an hour or more the circulation and respiration become very rapid, and the system in general is highly excited. Symptoms of debility subsequently ensue, followed by insensibility; and death occurs in six, ten, or twelve hours. On examination after death, the blood is found highly florid in every part of the body, and the heart acts strongly even after the breathing has ceased. For these experiments we are indebted to Broughton. Its eq. is = 8; eq. vol. = 50; symb. O.

THEORY OF COMBUSTION.

The only phenomena of combustion noticed by an ordinary observer, are the destruction of the burning body, and the developement of heat and light; but it has been demonstrated that in addition to these circumstances, oxygen gas invariably disappears, and a new compound consisting of oxygen and the combustible is generated. The term *combustion*, therefore, in its common signification, implies the rapid union of oxygen gas and combustible matter, accompanied with heat and light. As the evolution of heat and light is dependent on chemical action, the same phenomena may be expected in other chemical processes; and accordingly heat and light are frequently emitted quite independently of oxygen. Thus phosphorus takes fire, and a taper burns for a short time, in a vessel of chlorine; and several of the common metals, such as copper, antimony, and arsenic, in a state of fine division, become red hot when introduced into a jar of that gas. Potassium takes fire in cyanogen gas; and copper leaf or iron wire, if moderately heated, undergoes the same change in the vapour of sulphur. A mixture of iron filings and sulphur, when heated so as to bring the latter into perfect fusion, emits intense heat and light at the instant of combination; and a like effect, though in a far less degree, is produced by the action of concentrated sulphuric acid on pure magnesia. Most of these and similar examples, especially when one of the combining substances is gaseous, are frequently included under the idea of combustion; and they certainly belong to the same class of phenomena. In the subsequent observations, however, I shall employ the term in its ordinary sense; but the remarks concerning increase of temperature, whether with or without light, apply equally to all cases where heat is developed as a result of chemical action.

For many years prior to the discovery of oxygen gas, the phenomena of combustion were explained on the Stahlian or phlogistic hypothesis. All combustible bodies, according to Stahl, contain a certain principle which he called *phlogiston*, to the presence of which he ascribed their combustibility. He supposed that when a body burns, phlogiston escapes from it; and that when the body has lost phlogiston, it ceases to be combustible, and is then a dephlogisticated or incombustible substance. A metallic oxide was consequently regarded as a simple substance, and the metal itself as a compound of its oxide with phlogiston. The heat and light which accompany combustion, were attributed to the rapidity with which phlogiston is evolved during the process.

The discovery of oxygen proved fatal to the Stahlian doctrine. Lavoisier had the honour of overthrowing it, and of substituting in its place the antiphlogistic theory. The basis of his doctrine has already been stated,—that combustion and oxidation in general consist in the combination of combustible matter with oxygen. This fact he established beyond a doubt. On burning phosphorus in a jar of oxygen, he observed that a considerable quantity of the gas disappeared, that the phosphorus gained materially in weight, and that the increase of the latter exactly corresponded to the loss of the former. An iron wire was burnt in a similar manner, and the weight of the oxidized iron was found equal to that of the wire originally employed, added to the quantity of oxygen which had disappeared. That the oxygen is really present in the oxidized body he proved by a very decisive experiment. Some liquid mercury was confined in a vessel of oxygen gas, and exposed to a temperature sufficient for causing its oxidation. The oxide of mercury, so produced, was put into a small retort and heated to redness, when it was reconverted into oxygen and fluid mercury, the quantity of the oxygen being exactly equal to that which had combined with the mercury in the first part of the operation.

To account for the production of heat and light during combustion, Lavoisier had recourse to Black's Theory of latent heat.

Heat is always evolved when a substance, without change of form, passes from a rarer into a denser state, and also when a gas becomes liquid or solid, or a liquid solidifies; because a quantity of heat previously combined, or latent, within it, is then set free. Now this is precisely what happens in many instances of combustion. Thus water is formed by the burning of hydrogen, in which case two gases give rise to a liquid; and in forming phosphoric acid with phosphorus, or in oxidizing metals, oxygen is condensed into a solid. When the product of combustion is gaseous, as in the burning of charcoal, the evolution of heat is ascribed to the circumstance that the oxidized body contains a smaller quantity of combined heat, or has a smaller sp. heat, than the substances by which it is produced.

This is the weak point of Lavoisier's theory. Chemical action is very often accompanied by increase of temperature, and the heat evolved during combustion is only a particular instance of it. Any theory, therefore, by which it is proposed to account for the production of heat in some cases, ought to be applicable to all. When combustion, or any other chemical action, is followed by considerable condensation, in consequence of which the new body contains less insensible heat than its elements did before combination, it is obvious that heat will, in that case, be disengaged. But if this were the sole cause of the phenomenon, a rise of temperature should always be preceded by a corresponding diminution of sp. heat, and the extent of the former ought to be in a constant ratio with the degree of the latter. Now Petit and Dulong infer from their researches on this subject (An. de Ch. et Ph. x.), that the degree of heat developed during combination, bears no relation to the sp. heat of the combining substances; and that in the majority of cases, the evolution of heat is not attended by any diminution in the sp. heat of the compound. It is a well-known fact, that increase of temperature frequently attends chemical action, though the products contain much more insensible heat than the substances from which they were formed. This happens remarkably in the explosion of gunpowder, which is attended by intense heat; and yet its materials, in passing from the solid to the gaseous state, expand to at least 250 times their volume, and consequently render latent a large quantity of heat.

These circumstances leave no doubt that the evolution of heat during chemical action is owing to some cause quite unconnected with that assigned by Lavoisier; and if this cause operates so powerfully in some cases, it is fair to infer that part of the effect must be owing to it on those occasions, when the phenomena appear to depend on change of sp. heat alone. A new theory is therefore required to account for the chemical production of heat. But it is easier to perceive the fallacies of one doctrine, than to substitute another which shall be faultless; and it appears to me that chemists must, for the present, be satisfied with the simple statement, that energetic chemical action does of itself give rise to increase of temperature. Berzelius, in adopting the electro-chemical theory, regards the heat of combination as an electrical phenomenon, believing it to arise from the oppositely electrical substances neutralizing one another, in the same manner as the electric equilibrium is restored during the discharge of a Leyden jar. Electrical action certainly appears to be an essential part of every chemical change, and it is probable that the heat developed during the latter may be due to the former; but this part of science is as yet too imperfect for indicating the precise mode by which the effect is produced.

The heat emitted during combustion varies with the nature of the material. The effect of the combustible gases in raising the temperature of water, according to the experiments of Dalton, is shown in the following table.—(Chemical Philosophy, ii. 309.)

Hydrogen, in burning, raises an equal volume of water	5° F.
Carbonic oxide	4½
Light carburetted hydrogen	18
Olefiant gas	27
Coal gas, varies with the quality of the gas from	10 to 16
Oil gas, varies also with the quality of the gas from	12 to 20

Dalton further states that generally the combustible gases give out heat nearly in proportion to the oxygen which they consume.

Despretz has given a notice of some experiments on the heat developed in combustion (An. de Ch. et Ph. xxxvii. 180). The substances burned were hydrogen, carbon, phosphorus, and several metals; and so much of each was employed as to require the same quantity of oxygen. When the combustion of hydrogen gas produced 2578 degrees of heat, carbon gave out 2967, and iron 5325. Phosphorus, zinc, and tin, emit quantities of heat very nearly the same as iron. Hence it follows that, for equal quantities of oxygen, hydrogen in burning evolves less heat than most other substances. These results do not accord with those of Dalton.

SECTION IV.

HYDROGEN.

Hist.—First correctly described in 1766 by Cavendish (Phil. Trans. lvi. 144), under the name of *inflammable air*. It had been previously confounded with other combustible gases, and it was by some called *phlogiston*, from the notion that it is the matter of heat. Its present name is derived from *ὕδωϱ water*, and *γενναειν to generate.*

Prep.—Commonly in two ways. The first consists in passing the vapour of water over metallic iron heated to redness. This is done by putting iron wire into a gun-barrel open at both ends, to one of which is attached a retort containing pure water, and to the other a bent tube. The gun-barrel is placed in a furnace, and when it has acquired a full red heat, the water in the retort is made to boil briskly. The gas, which is copiously disengaged as soon as the steam comes in contact with the glowing iron, passes along the bent tube, and may be collected in convenient vessels, by dipping the free extremity of the tube into the water of a pneumatic trough. The second and more convenient method consists in putting pieces of iron or zinc into dilute sulphuric acid, formed of one part of strong acid and four or five of water. Zinc is generally preferred. The hydrogen obtained in these processes is not absolutely pure. The gas evolved during the solution of iron has an offensive odour, ascribed by Berzelius to the presence of a volatile oil, which may be almost entirely removed by transmitting the gas through alcohol. The oil appears to arise from some compound being formed between hydrogen and the carbon which is always contained even in the purest kinds of common iron; and it is probable that a little carburetted hydrogen gas is generated at the same time. The zinc of commerce contains sulphur, and almost always traces of charcoal, in consequence of which it is contaminated with hydro-sulphuric acid, and probably with the same impurities, though in a less degree, as are derived from iron. A little metallic zinc is also contained in it, apparently in combination with hydrogen. All these impurities, carburetted hydrogen excepted, may be removed by passing the hydrogen through a solution of pure potassa. To obtain hydrogen of great purity distilled zinc should be employed.

Prop.—Colourless, inodorous, tasteless; always gaseous when uncombined; a powerful refractor of light; the lightest body in nature, and hence the best material for filling balloons. From its extreme lightness it is difficult to ascertain its sp. gr. by weighing, because the presence of minute quantities of common air or watery vapour occasions considerable error. By the table of sp. gravities (page 173) it appears that hydrogen gas is just 16 times lighter than oxygen, an inference derived from the composition of water to be shortly stated: hence 100 C. I. 60° and 30 Bar. should weigh $\frac{1}{16} \times 34{\cdot}193 = 2{\cdot}1371$ grains, and its sp. gr. should be 0·06896.

It is neither acid nor alkaline. Water dissolves only $1\frac{1}{2}$ per cent. of its volume. It cannot support respiration: death ensues from deprivation of oxygen rather than from any noxious quality of the hydrogen, since an atmosphere composed of a due proportion of oxygen and hydrogen gases may be respired without inconvenience. Nor is it a supporter of combustion; for when a lighted candle, fixed on wire, is passed up into an inverted jar full of hydrogen gas, the light instantly disappears.

Hydrogen gas is inflammable in an eminent degree, though, like other combustibles, it requires the aid of a supporter of combustion, burning only where it is in contact with the air. Its combustion, when conducted in this manner, goes on tranquilly, and is attended with a yellowish blue flame and a very feeble light. The phenomena are different when the hydrogen is previously mixed with a due quantity of air. The approach of flame not only sets fire to the gas near it, but the whole is kindled at the same instant; and a flash of light passes through the mixture, followed by a violent explosion. The best proportion for the experiment is two measures of hydrogen to five or six of air. The explosion is far more violent when pure oxygen is used instead of atmospheric air, particularly when the gases are mixed together in the ratio of one measure of oxygen to two of hydrogen.

Oxygen and hydrogen gases cannot combine at ordinary temperatures, and may, therefore, be kept in a state of mixture without even gradual combination taking place between them. Hydrogen may be set on fire, when in contact with air or oxygen gas, by flame, by a solid body heated to bright redness, and by the electric spark. If a jet of hydrogen gas be thrown upon recently prepared spongy platinum, this metal almost instantly becomes red hot, and then sets fire to the gas, a discovery which was made in the year 1824 by Professor Doebereiner of Jena. The power of flame and electricity in causing a mixture of hydrogen with air or oxygen gas to explode, is limited. Mr. Cavendish found that flame occasions a very feeble explosion when the hydrogen is mixed with nine times its bulk of air; and that a mixture of four measures of hydrogen with one of air does not explode at all. An explosive mixture formed of two measures of hydrogen and one of oxygen gas, explodes from all the causes above enumerated. Biot found that sudden and violent compression likewise causes an explosion, apparently from the heat emitted during the operation; for an equal degree of condensation, slowly produced, has not the same effect. The electric spark ceases to cause detonation when the explosive mixture is diluted with twelve times its volume of air, fourteen of oxygen, or nine of hydrogen; or when it is expanded to sixteen times its bulk by diminished pressure. Spongy platinum acts just as rapidly as flame or the electric spark in producing explosion, provided the gases are quite pure and mixed in the exact ratio of two to one.* Mr. Faraday finds that platinum foil, if perfectly clean, produces gradual though rather rapid combination of the gases, often followed by explosion. (Phil. Trans. 1834.)

When the action of heat, the electric spark, and spongy platinum no longer cause explosion, a silent and gradual combination between the gases may still be occasioned by them. Sir H. Davy observed that oxygen and hydrogen gases unite slowly with one another, when they are exposed to a temperature above the boiling point of mercury, and below that at which glass begins to appear luminous in the dark. An explosive mixture diluted with air to too great a degree to explode by electricity, is made to unite silently by a succession of electric sparks. Spongy platinum causes them to unite slowly, though mixed with one hundred times their bulk of oxygen gas.

A large quantity of heat is evolved during the combustion of hydrogen gas. Lavoisier concludes from experiments made with his calorimeter (Elements, vol. i.), that one pound of hydrogen occasions as much heat in burning as is sufficient to melt 295·6 pounds of ice. Dr. Dalton fixes the quantity of ice at 320 pounds, and Dr. Crawford at 480. The most intense heat that can be produced, is caused by the combustion of hydrogen in oxygen gas. Dr. Hare of Philadelphia, who first burned hydrogen for this purpose, collected the gases in separate gas-holders, from which a stream was made to issue through tubes communicating with each other, just before their termination. At this point the jet of the mixed gases was inflamed. The effect of the combustion, though very great, is materially increased by forcing the two gases in due porportion into a strong metallic vessel by means of a condensing syringe, and setting fire to a jet of the mixture as it issues. An apparatus of this kind, now known by the name of the oxy-hydrogen blowpipe, was contrived by Mr. Newman, and employed by the late Professor Clarke in his experiments on the fusion of refractory substances. On opening a stop-cock which confines the compressed gases, a jet of the explosive mixture issues with force through a small blowpipe tube, at the extremity of which it is kindled. In this state, however, the apparatus should never be used; for as the reservoir is itself full of an explosive mixture, there is great danger of the flame running back along the tube, and setting fire to the whole gas at once. To prevent the occurrence of such an accident, which would most probably prove fatal to the operator, Professor Cumming proposed that the gas, as it issues from the reservoir, should be made to pass through a cylinder full of oil or water before reaching the point at which it is to burn; and Dr. Wollaston suggested the additional precaution of fixing successive layers of fine wire gauze within the exit tube, each of which would be capable of intercepting the communication of flame. A modification of this apparatus has been devised by Mr. Gurney; but both his and Newman's are rendered unnecessary by the safety tube lately proposed by Mr. Hemming. It consists of a brass cylinder, about 6 inches long, and 3-4ths of an inch wide, filled with very fine brass wire in length equal to that of the tube. A pointed rod of metal, 1-8th of an inch thick, is then forcibly inserted through the centre of the bundle of wires in the tube, so as to wedge them tightly together. The interstices between the wires thus constitute very fine metallic tubes, the conducting power of which is so great as entirely to intercept the passage of flame. The mixed gases are supplied from a common bladder. (Phil. Mag. 3rd S. i. 82.) A very intense heat may be safely and easily procured by passing a jet of oxygen gas through the flame of a spirit lamp, as proposed by the late Dr. Marcet. An elegant improvement on this principle has been devised by Mr. Daniell, by fixing a jet for conveying oxygen within another jet for hydrogen or coal gas, so that a current of oxygen may be introduced into the middle of the flame. (Phil. Mag. ii. 57. 3rd Series.) The heat from this apparatus is quite sufficient for most purposes; and it may be still further increased by causing the gases to pass separately through heated tubes, in order that they may have a temperature of 400° or 500° on issuing from the jets.—On this principle is founded the patent of Mr. Dunlop, of the Carron Iron Works, for increasing the temperature of blast furnaces: the air which supports the combustion is previously heated by transmission through iron tubes kept at a low red heat, whereby the power of the furnaces is surprisingly increased, and a great saving in fuel and time is accomplished.

---

* For a variety of facts respecting the causes which prevent the action of flame, electricity, and platinum in producing detonation, the reader may consult the Essay of M. Grotthus in the Ann. de Chimie, vol. lxxxii.; Sir H. Davy's work on Flame; Dr. Henry's Essay in the Philosophical Transactions for 1824; and a paper by myself in the Edinburgh Philosophical Journal for the same year.

Its eq. is = 1; eq. vol. = 100; Symb. H. Compounds with oxygen:—

	By Weight.			By Volume.	
	Hydrogen.	Oxygen.	Equiv.	Hyd.	Oxy.
Water (Protoxide of Hydrogen)	1 or 1 eq. +	8 or 1 eq. =	9	100	50
Peroxide of Hydrogen	1 or 1 eq. +	16 or 2 eq. =	17	100	100

Water.—First proved by Cavendish to be the sole product of the combustion of hydrogen gas. He demonstrated it by burning oxygen and hydrogen gases in a dry glass vessel, when a quantity of pure water was generated, exactly equal in weight to that of the gases which had disappeared. This experiment, which is the synthetic proof of the composition of water, was afterwards made on a much larger scale in Paris by Vauquelin, Fourcroy, and Seguin. Lavoisier first demonstrated its nature analytically, by passing a known quantity of watery vapour over metallic iron heated to redness in a glass tube. Hydrogen gas was disengaged, the metal in the tube was oxidized, and the weight of the former, added to the increase which the iron had experienced from combining with oxygen, exactly corresponded to the quantity of water decomposed.

Its composition by volume was demonstrated very satisfactorily by Nicholson and Carlisle: by resolving water into its elements by galvanism, and collecting them in separate vessels, they obtained precisely two measures of hydrogen and one of oxygen,—a result which has been fully confirmed by subsequent experimenters. The same fact was proved synthetically by Gay-Lussac and Humboldt, in their Essay on Eudiometry, published in the *Journal de Physique* for 1805. They found that when a mixture of oxygen and hydrogen is inflamed by the electric spark, those gases always unite in the exact ratio of one to two, whatever may be their relative quantity in the mixture. When one measure of oxygen is mixed with three of hydrogen, one measure of hydrogen remains after the explosion; and a mixture of two measures of oxygen and two of hydrogen leaves one measure of oxygen. When one volume of oxygen is mixed with two of hydrogen, both gases, if quite pure, disappear entirely on the electric spark being passed through them. The composition of water by weight was determined with great care by Berzelius and Dulong; and we cannot hesitate, considering the known dexterity of the operators, and the principle on which their method of analysis was founded, to regard their result as a nearer approximation to the truth than that of any of their predecessors. They state, as a mean of three careful experiments (Ann. de Ch. et Ph. xv.), that 100 parts of pure water consist of 11·1 of hydrogen and 88·9 oxygen, which is the ratio of 1 to 8·009, very nearly that of 1 to 8 above stated.

The processes for procuring a supply of hydrogen gas will now be intelligible. The first is the method by which Lavoisier made the analysis of water. It is founded on the fact that iron at a red heat decomposes water, the oxygen of that liquid uniting with the metal, and the hydrogen gas being set free. That the hydrogen which is evolved when zinc or iron is put into dilute sulphuric acid must be derived from the same source, is obvious from the consideration, that of the three substances, iron, sulphuric acid, and water, the last is the only one which contains hydrogen. The product of the operation, besides hydrogen, is sulphate of the protoxide of iron, if iron is used, or of the oxide of zinc, when zinc is employed, according to the following equation; $HO + SO_3 + Fe = FeO + SO_3 + H$. The knowledge of the combining proportions of these substances will readily give the exact quantity of each product. These numbers are —

Water (8 oxy. + 1 hyd.)	9
Sulphuric acid	40·1
Iron	28
Protoxide of iron (28 iron + 8 oxygen)	36
Sulphate of the protoxide of iron (40·1 + 36)	76·1

Hence for every 9 grains of water which are decomposed, 1 grain of hydrogen will be set free; 8 grains of oxygen will unite with 28 grains of iron, forming 36 of the protoxide of iron; and the 36 grains of protoxide will combine with 40·1 grains of sulphuric acid, yielding 76·1 of sulphate of the protoxide of iron. A similar calculation may be employed when zinc is used, merely by substituting the equivalent of zinc (32·5) for that of iron.—According to Mr.

Cavendish, an ounce of zinc yields 676 cubic inches, and an equal quantity of iron 782 cubic inches of hydrogen gas.

The action of dilute sulphuric acid on metallic zinc affords an instance of what was once called *Disposing Affinity*. Zinc decomposes pure water at common temperatures with extreme slowness; but as soon as sulphuric acid is added, decomposition of the water takes place rapidly, though the acid merely unites with oxide of zinc. The former explanation was, that the affinity of the acid for oxide of zinc disposed the metal to unite with oxygen, and thus enabled it to decompose water; that is, the oxide of zinc was supposed to produce an effect previous to its existence. The obscurity of this explanation arises from regarding changes as consecutive, which are in reality simultaneous. There is no succession in the process; the oxide of zinc is not formed previously to its combination with the acid, but at the same instant. There is, as it were, but one chemical change, which consists in the combination at one and the same moment of zinc with oxygen, and of oxide of zinc with the acid; and this change occurs because these two affinities, acting together, overcome the attraction of oxygen and hydrogen for one another.

Prop.—Transparent, colourless, inodorous, tasteless; powerful refractor of light; imperfect conductor of heat and electricity; very incompressible, its absolute diminution for a pressure of one atmosphere being only 51·3 millionths of its volume. (An. de Ch. et Ph. xxxvi. 140.) Its changes of form under varying temperatures have been already stated in the section on heat. Its sp. gr. is 1, being the unit to which the sp. gr. of all solids and liquids is referred as a convenient term of comparison. One cubic inch, at 62° and 30 Bar., weighs 252·458 grains. It is 815 times heavier than atmospheric air. The sp. gr. of aqueous vapour is 0·6202, and 100 C. I. (containing 100 hydrogen and 50 oxygen), at 212° and 30 Bar., weigh 14·96 grains; sp. gr. of ice is 0·92.

Owing partly to the extensive range of its own affinity, and partly to the nature of its elements, water is a chemical agent of great power. Of this, the preparation of hydrogen gas is an example; and indeed there are few complex changes, where oxygen and hydrogen are present, which do not give rise either to the production or decomposition of water. But, independently of the elements of which it is composed, it combines directly with many bodies. Sometimes it is contained in a variable ratio, as in ordinary solution; in other compounds it is present in a fixed definite proportion, as is exemplified by its union with several of the acids, the alkalies, and all salts that contain water of crystallization. These combinations are termed *hydrates.* Thus, concentrated sulphuric acid is a compound of one eq. of the real acid and one eq. of water; and its proper name is *hydrous sulphuric acid,* or *hydrate of sulphuric acid.* The prefix *hydro* has been sometimes used to signify the presence of water in definite proportion; but it is advisable, to prevent mistakes, to limit its employment to the compounds of hydrogen.

The purest water which can be found as a natural product, is procured by melting freshly fallen snow, or by receiving rain in clean vessels at a distance from houses. But this water is not absolutely pure; for if placed under the exhausted receiver of an air-pump, or boiled briskly for a few minutes, bubbles of gas escape from it. The air obtained in this way from snow water is much richer than atmospheric air in oxygen gas. According to Gay-Lussac and Humboldt it contains 34·8 per cent. of oxygen, and the air separated by ebullition from rain water contains 32 per cent. All water which has once fallen on the ground becomes impregnated with more or less earthy or saline matters, and can be separated from them only by distillation. The distilled water, thus obtained, and preserved in clean well-stopped bottles, is absolutely pure. Recently boiled water has the property of absorbing a portion of all gases, when its surface is in contact with them; and the absorption is promoted by brisk agitation. The following table, from Henry's Chemistry, shows the absorbability of different gases by water, deprived of all its air by ebullition.

100 C. I. water, at 60° and 30 Bar., absorb of

	Dalton and Henry.	Saussure.
Sulphuretted hydrogen	100 C. I.	253
Carbonic acid	100	106
Nitrous oxide	100	76
Olefiant gas	12·5	15·3
Oxygen	3·7	6·5
Carbonic oxide	1·56	6·2
Nitrogen	1·56	4·1
Hydrogen	1·56	4·6

The estimate of Saussure is in general too high. That of Dalton and Henry for nitrous oxide, according to the experiments of Davy, is considerably beyond the truth.

Its eq. is = 9; eq. vol. 100; symb. H + O, or HO, or H, or aq. from aqua.

Peroxide or Binoxide.—Discovered by Thenard in 1818. Its preparation is founded on the fact that there are two oxides of barium, the peroxide and protoxide, the former of which is converted into the protoxide by the action of acids. When this process is conducted with the necessary precautions, the oxygen which is set free, instead of escaping in the form of gas, unites with the hydrogen of the water, and brings it to a maximum of oxidation. For a full detail of all the minutiæ of the process, the reader may consult the original memoir of Thenard;[*] the general directions are the following:—To six or seven ounces of water add so much pure concentrated hydrochloric acid as is sufficient to dissolve 230 grains of baryta; and after having placed the mixed fluids in a glass vessel surrounded with ice, add in successive portions 185 grains of peroxide of barium reduced to powder, and stir with a glass rod after each addition. When the solution, which takes place without effervescence, is complete, sulphuric acid is added in sufficient quantity for precipitating the whole of the baryta in the form of an insoluble sulphate, leaving the hydrochloric acid in solution. Another portion of peroxide of barium, amounting to 185 grains, is then put into the liquid: the free hydrochloric acid instantly acts upon it, and as soon as it is dissolved, the baryta is again separated as a sulphate by the addition of sulphuric acid. The solution is then filtered, in order to separate the insoluble sulphate of baryta; and fresh quantities of peroxide of barium are added in succession, till about three ounces have been employed. The liquid then contains from 25 to 30 times its volume of oxygen gas. The hydrochloric acid which has served to decompose the peroxide of barium during the whole process, is now removed by the cautious addition of sulphate of oxide of silver, and the sulphuric acid afterwards separated by solid baryta.

Peroxide of hydrogen, as thus prepared, is still diluted with a considerable quantity of water. To separate the latter, the mixed liquids are placed, with a vessel of strong sulphuric acid, under the exhausted receiver of an air-pump. As the water evaporates, the density of the residue increases, till at last it acquires the sp. gr. of 1·452. The concentration cannot be pushed further; for if kept under the receiver after reaching this point, the peroxide itself gradually but slowly volatilizes without change.

Prop.—A colourless transparent liquid, inodorous, and of a metallic taste; volatilizes *in vacuo* less rapidly than water; retains its liquid form at all degrees of cold to which it has been exposed; at 59° is resolved into oxygen and water, and hence should be always kept in glass tubes surrounded by ice. It intermixes with water in all proportions; bleaches litmus and turmeric paper, whitens the skin and tongue, causing to both a pricking sensation, and thickens the saliva. The most remarkable of its properties is its facility of decomposition. Diffused daylight does not seem to exert any influence over it, and even the direct solar rays act upon it tardily. It effervesces from escape of oxygen at 59°, and the sudden application of a higher temperature, as that of 212°, gives rise to such rapid evolution of gas as to cause an explosion. Water, apparently by combining with the peroxide, renders it more permanent; but no degree of dilution can enable it to bear the heat of boiling water, at which temperature it is entirely decomposed. All the metals except iron, tin, antimony, and tellurium, have a tendency to decompose it, converting it into oxygen and water. A state of minute mechanical division is essential for producing rapid decomposition. If the metal is in mass, and the peroxide diluted with water, the action is slow. The metals which have a strong affinity for oxygen are oxidized at the same time, such as potassium, sodium, arsenic, molybdenum, manganese, zinc, tungsten, and chromium; while others, such as gold, silver, platinum, iridium, osmium, rhodium, palladium, and mercury, retain the metallic state.

---

[*] In the An. de Chim. et de Phys. vol. viii. ix. x. and l.; Annals of Philosophy, vol. xiii. and xiv.; and M. Thenard's Traité de Chimie.

It is decomposed at common temperatures by many of the metallic oxides. That some protoxides should have this effect, would be anticipated in consequence of their tendency to pass into a higher state of oxidation. The protoxides of iron, manganese, tin, cobalt, and others, act on this principle, and are really converted into peroxides. The peroxides of barium, strontium, and calcium may likewise be formed by the action of peroxide of hydrogen on baryta, strontia, and lime. But it is a singular fact, of which no satisfactory explanation has been given, that some oxides decompose it without passing into a higher degree of oxidation. The peroxides of lead, mercury, gold, platinum, manganese, and cobalt, possess this property in the greatest perfection, acting on peroxide of hydrogen, when concentrated, with surprising energy. The decomposition is complete and instantaneous; oxygen gas is evolved so rapidly as to produce a kind of explosion; and such intense temperature is excited, that the glass tube in which the experiment is conducted becomes red-hot. The reaction is very great even when the peroxide of hydrogen is diluted with water. Oxide of silver occasions very perceptible effervescence when put into water which contains only 1-50th of its bulk of oxygen. All the metallic oxides, which are decomposed by a red heat, such as those of gold, platinum, silver, and mercury, are reduced to the metallic state when they act upon peroxide of hydrogen. This effect cannot be altogether ascribed to heat disengaged during the action; for oxide of silver suffers reduction when put into a very dilute solution of the peroxide, although the decomposition is not then attended by an appreciable rise of temperature.

While the tendency of metals and metallic oxides is to decompose the peroxide of hydrogen, acids have the property of rendering it more stable. In proof of this, let a portion of that liquid, somewhat diluted with water, be heated till it begins to effervesce from the escape of oxygen gas; let some strong acid, as the nitric, sulphuric, or hydrochloric, be then dropped into it, and the effervescence will cease on the instant. When a little finely divided gold is put into a weak solution of peroxide of hydrogen, containing only 10, 20, or 30 times its bulk of oxygen, brisk effervescence ensues; but on letting one drop of sulphuric acid fall into it, effervescence ceases instantly; it is reproduced by the addition of potassa, and is again arrested by adding a second portion of acid. The only acids that do not possess this property are those that have a low degree of acidity, as carbonic and boracic acids; or those which suffer a chemical change when mixed with peroxide of hydrogen, such as hydriodic, hydrosulphuric, and sulphurous acids. Acids appear to increase the stability of the peroxide in the same way as water does, namely, by combining chemically with it. Several compounds of this kind were formed by Thenard, before he was aware of the existence of the peroxide of hydrogen. They were made by dissolving peroxide of barium in some dilute acid, such as the nitric, and then precipitating the baryta by sulphuric acid. As nitric acid was supposed under these circumstances to combine with an additional quantity of oxygen, Thenard applied the term oxygenized nitric acid to the resulting compound, and described several other new acids under a similar title. But the subsequent discovery of peroxide of hydrogen put the nature of the oxygenized acids in a clearer light; for their properties are easily explicable on the supposition that they are composed, not of acids and oxygen gas, but of acids united with peroxide of hydrogen.

Peroxide of hydrogen was analysed by diluting a known weight of it with water, and then decomposing it by boiling the solution.

Its eq. is $=17$; symb. $H+2O$, or HO_2, or $\ddot{H}$.

SECTION V.

NITROGEN.

Hist.—First noticed by Rutherford of Edinburgh in 1772. Discovered to be a constituent of the atmosphere by Lavoisier in 1775, and by Scheele about the same time. It was termed azote (α privative, and *ζωη life*,) by Lavoisier, from its inability to support respiration. The name of nitrogen is derived from its being an element of nitric acid.

Prep.—1. By burning a piece of phosphorus in a jar full of air inverted over water. The strong affinity of phosphorus for oxygen enables it to burn till the whole of that gas is consumed. The product of the combustion, metaphosphoric acid, is at first diffused through the residue in the form of a white cloud; but as this substance is rapidly absorbed by water, it disappears entirely in the course of half an hour. The residual gas is nitrogen, containing a small quantity of carbonic acid and vapour of phosphorus, both of which may be removed by agitating it briskly with a solution of pure potassa. Several other substances may be employed for withdrawing oxygen from atmospheric air. A solution of protosulphate of iron, charged with binoxide of nitrogen, absorbs the oxygen in the space of a few minutes. A stick of phosphorus produces the same effect in twenty-four hours, if exposed to a temperature of 60°. A solution of sulphuret of potassium or calcium acts in a similar manner; and a mixture of equal parts of iron filings and sulphur, made into a paste with water, may be employed with the same intention. Both these processes, however, are inconvenient from their slowness.—2. By exposing a mixture of fresh muscle and nitric acid of sp. gr. 1·20 to a moderate temperature. Effervescence then takes place, and a large quantity of gaseous matter is evolved, which is nitrogen mixed with a little carbonic acid. The latter must be removed by agitation with lime water; but the residue still retains a peculiar odour, indicative of the presence of some volatile principle which cannot be wholly separated from it. The theory of this process is somewhat complex, and will be considered more conveniently in a subsequent part of the work.

3. By transmitting chlorine gas through a solution of ammonia, when that alkali yields its hydrogen to the chlorine, and its nitrogen is evolved.

Prop.—Colourless, tasteless, inodorous; always gaseous when uncombined; sp. gr. 0·9722, so that 100 C.I. weigh 30·166 grains; no action on the blue colour of plants; water dissolves 1½ per cent. It is distinguished from other gases more by negative characters than by any striking quality. It is not a supporter of combustion; but, on the contrary, extinguishes all burning bodies that are immersed in it. No animal can live in it; but yet it exerts no injurious action either on the lungs or on the system at large, the privation of oxygen gas being the sole cause of death. It is not inflammable like hydrogen; though, under favourable circumstances, it may be made to unite with oxygen.

Considerable doubt exists as to the nature of nitrogen. Though ranked among the simple non-metallic bodies, some circumstances have led to the suspicion that it is compound; and this opinion has been warmly advocated by Davy and Berzelius. The chief argument in favour of this view is drawn from the phenomena that attend the formation of what is called the *ammoniacal amalgam.* From the metallic appearance of this substance, it was supposed to be a compound of mercury and a metal; and as the only method of forming it is by the action of galvanism on a salt of ammonia, in contact with a globule of mercury, it follows that the metal, if present at all, must have been supplied by the ammonia. Now ammonia is composed of hydrogen and nitrogen; and as the former, from its small sp. gravity, can hardly be supposed to contain a metal, it was inferred that it must be present in the latter. Unfortunately for this argument, the supposed metal cannot be obtained in a separate state. The amalgam no sooner ceases to be under galvanic influence than its elements begin to separate spontaneously, and in a few minutes decomposition is complete, the sole products being ammonia, hydrogen, and pure mercury. Davy accounted for this change on the supposition that water is decomposed; that its oxygen reproduces nitrogen by uniting with the supposed metal; and that one part of its hydrogen forms ammonia by uniting with the nitrogen, while the remainder escapes in the form of gas. But Gay-Lussac and Thenard (Recherches Physico-Chimiques, vol. i.) declare that the amalgam resolves itself into mercury, ammonia, and hydrogen, even though perfectly free from moisture; and they infer from their experiments that it is composed of those three substances combined directly with each other. It hence appears that the examination of the ammoniacal amalgam affords no proof of the compound nature of nitrogen; nor was Davy's attempt to decompose that gas by aid of potassium, intensely heated by a galvanic current, attended with better success.

Its eq. is 14·15; eq. vol. = 100; symb. N.

The compounds of nitrogen treated of in this section are the following, exclusive of atmospheric air, which is regarded as a mechanical mixture:—

	By volume.		By weight.			
	Nit.	Oxy.	Nit.	Oxy.	Equiv.	Formulæ.
Nitrous oxide	100	50	14·15	+8	=22·15	$N+O$
Nitric oxide	100	100	14·15	+16	=30·15	$N+2O$
Hyponitrous acid	100	150	14·15	+24	=38·15	$N+3O$
Nitrous acid	100	200	14·15	+32	=46·15	$N+4O$
Nitric acid	100	250	14·15	+40	=44·15	$N+5O$

ON THE ATMOSPHERE.

The earth is everywhere surrounded by a mass of gaseous matter called the atmosphere, which is preserved at its surface by the force of gravity, and revolves together with it around the sun. It is colourless and invisible, excites neither taste nor smell when pure, and is not sensible to the touch unless when it is in motion. It possesses the physical properties of elastic fluids in a high degree. Its sp. gr. is unity, being the standard with which the density of all gaseous substances is compared. At 30 Bar. and 32° it is 769·4 times lighter than water, and 10462 than mercury; or at 62°, 815 times lighter than water, and nearly 11065 times lighter than mercury. The knowledge of its exact weight is an essential element in many physical and chemical researches, and has been determined with very great care by Prout, who finds that 100 C. I. of pure and dry atmospheric air, at 60° and 30 Bar. weigh 31·0117 grains.

The pressure of the atmosphere was first noticed early in the 17th century by Galileo, and was afterwards demonstrated by his pupil Torricelli, to whom science is indebted for the invention of the barometer. Its pressure at the level of the sea is equal to a weight of about 15 pounds on every square inch of surface, and is capable of supporting a column of water 34 feet high, and one of mercury of 30 inches; that is, a column of mercury of one inch square and 30 inches long has the same weight (nearly 15 pounds) as a column of water of equal base and 34 feet long, and as a column of air of equal base reaching from the level of the sea to the extreme limit of the atmosphere. By the use of the barometer it was discovered that the atmospheric pressure is variable. It varies according to the elevation above the level of the sea, and on this principle the height of mountains is estimated. Supposing the density of the atmosphere to be uniform, a fall of one inch in the barometer would correspond to 11065 inches, or 922 feet of air; but in order to make the calculation with accuracy, allowance must be made for the increasing rarity of the air, and for various other circumstances which are detailed in works on meteorology. (Daniel's Meteorological Essays, 2nd edit. 376.) From causes at present not understood, the pressure varies likewise at the same place. On this depends the indications of the barometer as a weather-glass; for observation has fully proved, that the weather is commonly fair and calm when the barometer is high, and usually wet and stormy when the mercury falls.

Atmospheric air is highly compressible and elastic, so that its particles admit of being approximated to a great extent by compression, and expand to an extreme degree of rarity, when the tendency of its particles to separate is not restrained by external force. The volume of air and all other gaseous fluids, so long as they retain the elastic state, is inversely as the pressure to which they are exposed. Thus a portion of air which occupies 100 measures when compressed by a force of one pound, will be diminished to 50 measures when the pressure is doubled, and will expand to 200 measures when the compression is equal to half a pound. This law was first demonstrated in 1662 by the celebrated Boyle, and a second demonstration of it was given some years afterwards by the French philosopher Mariotte, apparently without being aware that the discovery had been previously made in England. It is hence frequently called the law of Mariotte. Till lately it had not been verified for very great pressures; but from the experiments of Oersted in 1825, who extended his observations to air compressed by a force equal to 110 atmospheres, it may be inferred to be quite general, except when the gaseous matter assumes the liquid form. (Ed. Journal of Science, iv. 224.) Gases vary from this law when they approach the point at which they assume the liquid form. At what pressure air becomes liquid is uncertain, since all attempts to condense it have hitherto been unsuccessful.

The extreme compressibility and elasticity of the air accounts for the facility with which it is set in motion, and the velocity with which it is capable of moving. It is subject to the laws which characterize elastic fluids in general. It presses, therefore, equally on every side; and when some parts of it become lighter than the surrounding portions, the denser particles rush rapidly into their place and force the more rarefied ones to ascend. The motion of air gives rise to various familiar phenomena. A stream or current of air is wind, and an undulating vibration excites the sensation of sound.

The atmosphere is not of equal density at all its parts. This is obvious, from the consideration that those portions which are next the earth sustain the whole pressure of the atmosphere, while the higher strata bear only a part. The atmospheric column diminishes in length as the distance from the earth's surface increases; and, consequently, the greater the elevation, the lighter must be the air. It is not known to what height the atmosphere extends. From calculations founded on the phenomena of refraction, its height is supposed to be about 45 miles; and Wollaston estimated, from the law of expansion of gases, that it must extend to at least 40 miles with properties unimpaired by rarefaction. In speculating on its extent beyond that distance, it becomes a question whether the atmosphere is or is not limited to the earth. This subject was discussed with his usual sagacity by Wollaston in an Essay on the Finite Extent of the Atmosphere (Phil. Trans. 1822). Supposing the atmosphere unlimited, it should pervade all space, and accumulate about the sun, moon, and planets, forming around each an atmosphere, the density of which would depend on their respective forces of attraction. Now Wollaston inferred from astronomical observations made by himself and Kater, that there is no solar atmosphere; and the observations of other astronomers appear to justify the same inference with respect to the planet Jupiter. If the accuracy of these conclusions be admitted, it follows that our atmosphere is confined to the earth; and it may next be asked, by what means is its extent limited? Wollaston accounted for it by supposing the air, after attaining a certain degree of rarefaction, to possess such feeble elasticity, that the tendency of its particles to separate further from each other is counteracted by gravity. The unknown height at which this equilibrium between the two forces of elasticity and gravitation takes place, is the extreme limit of the atmosphere. The loss of elasticity may be ascribed to two powerful and concurring causes; namely, to the distance between the particles of air when highly rarefied, and to the extreme cold which prevails in the higher strata of the atmosphere.

The temperature of the atmosphere varies with its elevation. Gaseous fluids permit radiant matter to pass freely through them without any absorption, and therefore without their temperature being influenced by its passage. The atmosphere is not heated by transmitting the rays of the sun, but receives its heat solely from the earth, and chiefly by actual contact; so that its temperature becomes progressively lower, as the distance from the general mass of the earth increases. Another circumstance which contributes to the same effect, is the increasing tenuity of the atmosphere; for the temperature of rarefied air is less raised by a given quantity of heat, than that of the same portion of air when compressed, owing to its sp. heat being greater in the former state than in the latter. From the joint influence of both these causes it is found that, in ascending into the atmosphere, the temperature diminishes at the rate of one degree for about every 352 feet. The rate of decrease is probably much slower at considerable distances from the earth; but still there is no reason to doubt that the temperature continues to decrease with the increasing elevation. There must consequently, in every latitude, be a point where the thermometer never rises above 32°, and where ice is never liquefied. This point varies with the latitude, being highest within the tropics, and descending gradually as we advance towards the poles. The following table, from the Supplement to the Encyclopedia Britannica, page 190, article Climate, shows the point of perpetual ice corresponding to different latitudes:—

Latitude.	English feet in height.	Latitude.	English feet in height.
0°	15,207	45°	7,671
5°	15,095	50°	6,334
10°	14,764	55°	5,034
15°	14,220	60°	3,818
20°	13,478	65°	2,722
25°	12,557	70°	1,778
30°	11,484	75°	1,016
35°	10,287	80°	457
40°	9,001	85°	117

Air was one of the four elements of the ancient pilosophers, and their opinion of its nature prevailed generally, till its accuracy was rendered questionable by the experiments of Boyle, Hooke, and Mayow. The discovery of oxygen gas in 1774 paved the way to the knowledge of its real composition, which was discovered about the same time by Scheele and Lavoisier. The former exposed some atmospheric air to a solution of sulphuret of potassium, which gradually absorbed the whole of the oxygen. Lavoisier effected the same object by the combustion of iron wire and phosphorus.

The earlier analyses of the air did not agree very well with each other. According to the researches of Lavoisier, it is composed of 27 measures of oxygen and 73 of nitrogen. The analysis of Scheele gave a somewhat higher proportion of oxygen. Priestley found that the quantity of oxygen varies from 20 to 25 per cent.; and Cavendish estimated it only at 20. These discrepancies must have arisen from imperfections in the mode of analysis; for the proportion of oxygen has been found by subsequent experiments to be almost, if not exactly, that which was stated by Cavendish. The results of Scheele and Priestley are clearly referable to this cause. It is now known that the processes they employed cannot be relied on, unless certain precautions are taken of which those chemists were ignorant. Recently boiled water absorbs nitrogen; and, consequently, if sulphuret of potassium be dissolved in that liquid by the aid of heat, the solution, when agitated with air, takes up a portion of nitrogen, and thereby renders the apparent absorption of oxygen too great. This inconvenience may be avoided by dissolving the sulphuret in cold unboiled water. Binoxide of nitrogen, employed by Priestley, removes all the oxygen in the course of a few seconds; but for reasons which will soon be mentioned, its indications are apt to be fallacious. The combustion of phosphorus, as well as the gradual oxidation of that substance, acts in a very uniform manner, and removes the whole of the oxygen completely. The residual nitrogen contains a little of the vapour of phosphorus, which increases the bulk of that gas by 1-40th, for which an allowance must be made in estimating the real quantity of nitrogen.

Since chemists have learned the precautions to be taken in the analysis of the air, a close correspondence has been observed in the results of their experiments upon it. The researches of Davy, Dalton, Gay-Lussac, Thomson, and others, leave no doubt that 100 measures of pure atmospheric air consist of 20 or 21 volumes of oxygen, and 80 or 79 of nitrogen. The most approved mode of analysis consists in mixing with the air a quantity of hydrogen sufficient to convert all the oxygen present into water, and kindling the mixture by the electric spark. The combination may also be effected without detonation by means of spongy platinum. Water is formed, and is condensed; and since that liquid is composed of one volume of oxygen and two of hydrogen, one-third of the diminution must give the exact quantity of oxygen. This process is so easy of execution, and so uniform in its indications, that it is now employed nearly to the total exclusion of all others.

Such is the constitution of pure atmospheric air. But the atmosphere is never absolutely pure; for it always contains a certain variable quantity of carbonic acid and watery vapour, besides the odoriferous matter of flowers and other volatile substances, which are also frequently present. Saussure found carbonic acid in air collected at the top of Mont Blanc; and it exists at all altitudes which have been hitherto attained. Saussure, in a recent essay, states the proportion of this gas to vary at the same place within short intervals of time. It is greater in summer than in winter; and from observations made during spring, summer, and autumn, in the open fields, and in calm weather, its proportion is inferred to be always greater at night than in the day, and to be more abundant in gloomy than in bright weather. A very moist state of the ground, as after much rain, diminishes the quantity of carbonic acid, apparently by direct absorption. It is rather more abundant in elevated situations, as on the summits of high mountains, than in the plains; but its quantity is there nearly the same in day and night, in wet and dry weather, because the higher strata of the air are less influenced by vegetation, and the state of the soil. Saussure thinks also that a highly electrical state of the atmosphere tends to diminish the quantity of carbonic acid. He found that 10,000 parts of air contain 4·9 of carbonic acid as a mean, 6·2 as a maximum, and 3·7 as a minimum. (An. de Ch. et Ph. xxxviii. 411. xliv. 5.)

The chief chemical properties of the atmosphere are owing to the presence of oxygen gas. Air from which this principle has been withdrawn is nearly inert. It can no longer support respiration and combustion, and metals are not oxidized by being heated in it. Most of the spontaneous changes which mineral and dead organized matters undergo, are owing to the powerful affinities of oxygen. The uses of the nitrogen are in a great measure unknown. It was supposed to act as a mere diluent to the oxygen; but it most probably serves some useful purpose in the economy of animals, the exact nature of which has not been discovered.

The knowledge of the composition of the air, and of the importance of oxygen to the life of animals, naturally gave rise to the notion that the healthiness of the air, at different times, and in different places, depends on the relative quantity of this gas. It was therefore supposed that the purity of the atmosphere, or its fitness for communicating health and vigour, might be discovered by determining the proportion of oxygen; and hence the origin of the term *Eudiometer*, which was applied to the apparatus for analyzing the air. But this opinion, though at first supported by the discordant results of the earlier analysts, was soon proved to be fallacious. On the contrary, the composition of the air is not only constant in the same place, but is the same in all regions of the earth, and at all altitudes. Air collected at the summit of the highest mountains, such as Mont Blanc and Chimborazo, contains the same proportion of oxygen as that of the lowest valleys. The air of Egypt was found by Berthollet to be similar to that of France. The air which Gay-Lussac brought from an altitude of 21,735 feet above the earth, had the same composition as that collected at a short distance from its surface. Even the miasms of marshes, and the effluvia of infected places, owe their noxious qualities to some principle of too subtile a nature to be detected by chemical means, and not to a deficiency of oxygen. Seguin examined the infectious atmosphere of an hospital, the odour of which was almost intolerable, and could discover no appreciable deficiency of oxygen, or other peculiarity of composition.

The question has been much discussed, whether the oxygen and nitrogen gases of the atmosphere are simply intermixed, or chemically combined with each other. Appearances are at first view greatly in favour of the latter opinion. Oxygen and nitrogen gases differ in density, and therefore it might be expected, were they merely mixed together, that the oxygen as the heavier gas ought, in obedience to the force of gravity, to collect in the lower regions of the air; while the nitrogen should have a tendency to occupy the higher. But this has nowhere been observed. If air be confined in a long tube preserved at perfect rest, its upper part will contain just as much oxygen as the lower, even after an interval of many months; nay, if the lower part of it be filled with oxygen, and the upper with nitrogen, these gases will be found in the course of a few hours to have mixed intimately with one another. The constituents of the air are, also, in the exact proportion for combining. By measure they are nearly in the simple ratio of 1 to 4, which agrees with the law of combination by volume; and by weight they are as 8 to 28, which corresponds to 1 eq. of oxygen and 2 of nitrogen.

Strong as are these arguments in favour of the chemical theory, it is nevertheless liable to objections which appear insuperable. The atmosphere possesses all the characters that should arise from a mechanical mixture. There is not, as in all other cases of chemical union, any change in the bulk, form, or other qualities of its elements. The nitrogen manifests no attraction for the oxygen. All bodies which have an affinity for oxygen abstract it from the atmosphere with as much facility as if the nitrogen were absent altogether. Even water effects this separation; for the air which is expelled from rain water by ebullition, contains more than 21 per cent. of oxygen. When oxygen and nitrogen gases are mixed together in the ratio of 1 to 4, the mixture occupies precisely 5 volumes, and has every property of pure atmospheric air. The refractive power of the atmosphere is precisely such as a mixture of oxygen and nitrogen gases ought to possess; and different from what would be expected were its elements chemically united. (Edinburgh Journal of Science, iv. 211.)

Since the elements of the air cannot be regarded as in a state of actual combination, it is necessary to account for the steadiness of their proportion on some other principle. It has been conceived that the affinity of oxygen and nitrogen for one another, though insufficient to cause their combination when mixed together at ordinary temperatures, might still operate in such a manner as to prevent their separation; that a certain degree of attraction is even then exerted between them, which is able to counteract the tendency of gravity. An opinion of this kind was advanced by Berthollet, in his *Statique Chimique*, and defended by Murray. This doctrine, however, is not satisfactory. It is conceivable that oxygen and nitrogen may attract each other in the way supposed; and it may be admitted that this supposition explains why these two gases continue in a state of perfect mixture. But still the explanation is unsatisfactory; and for the following reason:—Dalton took two cylindrical vessels, one of which was filled with carbonic acid, the other with hydrogen gas; the latter was placed perpendicularly over the other, and a communication was established between them. In the course of a few hours hydrogen was detected in the lower vessel, and carbonic acid gas in the upper. If the upper vessel be filled with oxygen, nitrogen, or any other gas, the same phenomena will ensue: the gases will be found, after a short interval, to be in a state of mixture, and will at last be distributed equally through both vessels. Now this result cannot be ascribed to the action of affinity. Carbonic acid cannot be made to unite either with hydrogen, oxygen, or nitrogen; and therefore, it is gratuitous to assert that it has an affinity for them. Some other power must be in operation, capable of producing the mixture of gases with each other, independently of chemical attraction; and if this power can cause carbonic acid to ascend through a gas which is twenty-two times lighter than itself, it will surely explain why oxygen and nitrogen gases, the densities of which differ so little, should be intermingled in the atmosphere.

The explanation which Dalton has given of these phenomena is founded on the assumption, that the particles of one gas, though highly repulsive to each other, do not repel those of a different kind. Hence one gas should act as a vacuum with respect to another; and if a vessel full of carbonic acid communicate with another of hydrogen, the particles of each gas should insinuate themselves between the particles of the other, till they are equally diffused through both vessels. The particles of the carbonic acid do not indeed fill the space occupied by the hydrogen with the same velocity as if it were a real vacuum, because the particles of the hydrogen afford a mechanical impediment to their progress. The ultimate effect, however, is the same as if the vessel of hydrogen had been a vacuum. (Manchester Memoirs, vol. v.)

Though it would not be difficult to find objections to this hypothesis, it has the merit of being applicable to every possible case; which cannot, I conceive, be admitted of the other. It accounts not only for the mixture of gases, but for the equable diffusion of vapours through gases, and through each other. This view receives support from Graham's experiments on the diffusion of gases. (Phil. Trans. Edin. 1831.) When a gas is contained in a glass bell jar which has a crack or fissure in its sides, or communicates with the air by a narrow aperture, or is contained in a porous vessel, the gas gradually diffuses itself into the air, and air into the gas, each passing through the chink or other small opening at the same time, but in opposite directions. On ascertaining after an interval how much gas has escaped from, and how much air entered into, the vessel, it will be found that the respective quantities depend on the relative sp. gravities; and the same principle of intermixture equally applies when the apertures of communication are large, as when they are small. Each gas has a diffusiveness peculiar to itself, and which is greater as its sp. gr. is less. Graham determined the rate of diffusion for different gases by means of what he calls a *diffusion tube*, which is simply a graduated tube closed at one end by plaster of Paris, a substance, when moderately dry, possessed of the requisite porosity. He has been led by direct experiment to the following conclusion,—that "the diffusion or spontaneous intermixture of two gases in contact, is effected by an interchange in position of indefinitely small volumes of the gases, which volumes are not necessarily of equal magnitude, being, in the case of each gas, inversely proportional to the square root of the density of that gas." The relative diffusiveness of each gas may hence be represented by the reciprocal of the square root of its sp. gr. Thus, the sp. gr. of air being 1, its diffusiveness is 1 also; that of hydrogen is

$$\frac{1}{\sqrt{0{\cdot}069}} = \frac{1}{0{\cdot}2627} = 3{\cdot}807; \text{ that of oxygen } \frac{1}{\sqrt{1{\cdot}102}} = \frac{1}{1{\cdot}05} = 0{\cdot}9524;$$

$$\text{and that of nitrogen } \frac{1}{\sqrt{0{\cdot}972}} = 1{\cdot}014;$$

so that the relative power of diffusion of air, hydrogen, oxygen, and nitrogen, is indicated by the numbers, 1, 3·807, 0·9524 and 1·014. In gases which are very sparingly soluble in water, and hence not condensable by the moisture of the plaster of Paris, the results of experiment coincide so exactly with the law, that Graham suggests its application to determine the sp. gr. of gases. Thus if g denote the diffusiveness of a gas, as found by careful experiment, and d its sp. gr.; then since, by the law of diffusion,

$$g = \frac{1}{\sqrt{d}}, \text{ we have } d = \frac{1}{g^2}.$$

It is obvious that these phenomena cannot be referred to any chemical principle, but are dependent on the mechanical constitution of gases. It has been lately shown in a very clever paper by T. Thomson of Clitheroe (Phil. Mag. 3rd Series, iv. 321), that the law of gaseous diffusion is included under Dalton's hypothesis, that one gas is as a vacuum with respect to another. For it is a law deduced from the physical properties of gaseous bodies, that the velocities of gases flowing under like circumstances into a vacuum are inversely as the square roots of their sp. gravities, which is precisely the same law that regulates their flow into each other.

There is still one circumstance for consideration respecting the atmosphere. Since oxygen is necessary to combustion, to the respiration of animals, and to various other natural operations, by all of which that gas is withdrawn from the air, it is obvious that its quantity would gradually diminish, unless the tendency of those causes were counteracted by some compensating process. To all appearance there does exist some source of compensation; for chemists have not hitherto noticed any change in the constitution of the atmosphere. The only source by which oxygen is known to be supplied, is the action of growing vegetables. A healthy plant absorbs carbonic acid during the day, appropriates the carbonaceous part of that gas to its own wants, and evolves the oxygen with which it was combined. During the night, indeed, an opposite effect is produced. Oxygen gas then disappears, and carbonic acid is eliminated; but it follows from the experiments of Priestley, Davy, and Daubeny, that plants during 24 hours yield more oxygen than they consume. Whether living vegetables make a full compensation for the oxygen removed from the air by the processes above mentioned, is uncertain. From the great extent of the atmosphere, and the continual agitation to which its different parts are subject by the action of winds, the effects of any deteriorating process would be very gradual, and a change in the proportion of its elements could be perceived only by observations made at very distant intervals.

Besides oxygen, nitrogen, carbonic acid, and traces of volatile organic substances, air, as already stated, always contains a greater or less amount of the vapour of water. The methods and instruments employed for determining its quantity have been described in the article Evaporation. As these instruments are termed hygrometers, the moisture of the atmosphere is often called hygrometric; and solid substances which absorb it are said to contain hygrometric water.

PROTOXIDE OF NITROGEN.

Hist.—Dephlogisticated air of Priestley, its discoverer; and the nitrous oxide of Davy, who studied it minutely. (Researches on the Nitrous Oxide, 1800.)

Prep.—It may be formed by exposing nitric oxide for some days to the action of iron filings, or other substances which have a strong affinity for oxygen, when the nitric oxide loses one half of its oxygen, and is converted into the protoxide; but the most convenient method is by nitrate of ammonia. This salt is prepared by neutralizing with carbonate of ammonia pure nitric acid diluted with about three parts of water, and concentrating by evaporation until a drop of the liquid let fall on a cold plate becomes a firm mass, adding a little ammonia towards the close to ensure neutrality. The salt after cooling is broken to pieces, introduced into a retort, and heated by a lamp or pan of charcoal: at first, below 400°, fusion ensues; and as the heat rises to 480° or 500°, rapid decomposition sets in, which continues until all the salt disappears. If a white cloud appears within the retort, due to some of the salt subliming undecomposed, the heat should be checked.

The sole products of this operation, when carefully conducted, are water and protoxide of nitrogen. The nature of the change will be readily understood by comparing the composition of nitrate of ammonia with that of the products derived from it. These, in round numbers, are as follows:—

Nitric Acid.	Ammonia.	Water.	Prot. of Nitrogen.
Nitrogen 14 or 1 eq.	Nitrogen 14 or 1 eq.	Hyd. 3 or 3 eq.	Nit. 28 or 2 eq.
Oxygen 40 or 5 eq.	Hydrogen 3 or 3 eq.	Oxy. 24 or 3 eq.	Oxy. 16 or 2 eq.
54	17	27	44

The same expressed in symbols is

$$NH_3 + NO_5 = 3HO + 2NO.$$

It thus appears that the hydrogen in the ammonia takes so much oxygen as is sufficient for forming water, and the residual oxygen converts the nitrogen both of the nitric acid and of the ammonia into protoxide of nitrogen: 71 grains of the salt will thus yield 44 grains of protoxide of nitrogen and 27 of water.

Prop.—Colourless, slightly agreeable odour, and sweetish taste; commonly gaseous, but at 45° and under a pressure of 50 atmospheres it is liquid; sp. gr. of the gas = 1·5241, and 100 C. I. weigh 47·22 grains; no action on test paper. Recently boiled water at 60° dissolves nearly its own volume of the gas, and yields it unchanged by boiling: hence it cannot be preserved over cold water, and may by it be separated from gases which are insoluble in water. It is a supporter of combustion. Most substances burn in it with far greater energy than in the atmosphere. When a recently extinguished candle with a very red wick is introduced into it, the flame is instantly restored. Phosphorus, if previously kindled, burns in it with great brilliancy. Sulphur, when burning feebly, is extinguished by it; but if immersed while the combustion is lively, the size of the flame is considerably increased. With an equal bulk of hydrogen it forms a mixture which explodes violently by the electric spark or by flame. In all these cases the product of combustion is the same as when oxygen gas or atmospheric air is used. The protoxide is decomposed; the combustible matter unites with its oxygen, and the nitrogen is set free. It suffers decomposition when a succession of electric sparks is passed through it, and a similar effect is caused by conducting it through a porcelain tube heated to incandescence. It is resolved, in both instances, into nitrogen, oxygen, and nitrous acid.

Davy discovered that it may be taken into the lungs with safety, and that it supports respiration for a few minutes. He breathed 9 quarts of it, contained in a silk bag, for three minutes, and 12 quarts for rather more than four; but no quantity could enable him to bear the privation of atmospheric air for a longer period. Its action on the system, when inspired, is very remarkable. A few deep inspirations are followed by most agreeable feelings of excitement, similar to the earlier stages of intoxication. This is shown by a strong propensity to laughter, by a rapid flow of vivid ideas, and an usual disposition to muscular exertion. These feelings, however soon subside; and the person returns to his usual state without experiencing the languor or depression which so universally follows intoxication from spirituous liquors. Its effects, however, on different persons, are various; and in individuals of a plethoric habit it sometimes produces giddiness, headache, and other disagreeable symptoms.

When 100 measures of it are mixed with 100 of hydrogen and fired by electricity, 100 of nitrogen gas remain, and the sole other product is water. As 100 of hydrogen unite with 50 of oxygen, it follows that 100 measures of the protoxide contain 100 of nitrogen and 50 of oxygen gases. This result, obtained by Davy, has been confimed by Henry, who analyzed it by means of carbonic oxide gas (An. Phil. N. S. viii. 299). Now,

100 cubic inches of nitrogen gas weigh . .	30·166 grains
50 do. oxygen	17·054
These numbers added together amount to . .	47·220

which must be the weight of 100 C. I. of the protoxide. Its composition by weight is determined by the same data, being 17·054 oxygen to 30·166 nitrogen, or 8 to 14 nearly, as already stated. Its eq. is = 22·15; eq. vol. = 100; symb. N + O, NO, or N.

BINOXIDE OF NITROGEN.

Hist.—Discovered by Hales, but first carefully studied by Priestley, under the name of *nitrous gas.* It is also called *nitric oxide*, and *deutoxide of nitrogen.*

Prep.—Preferably by the action of nitric acid, of sp. gr. 1·2, on metallic copper. Brisk effervescence takes place without the aid of heat, and the gas may be collected over water or mercury. The copper gradually disappears during the process; the liquid acquires a beautiful blue colour, and yields on evaporation a salt which is composed of nitric acid and oxide of copper. The chemical changes that occur are the following:—One portion of nitric acid suffers decomposition: part of its oxygen oxidizes the copper; while another part is retained by the nitrogen of the nitric acid, forming binoxide of nitrogen. The oxide of copper attaches itself to some undecomposed nitric acid, and forms the blue nitrate. Many other metals are oxidized by nitric acid, with disengagement of a similar compound; but none, mercury excepted, yields so pure a gas as copper. The following equation expresses the reaction:—

$$Cu_3 + 4\,N\,O_5 = 3\,(Cu\,O, N\,O_5) + N\,O_2.$$

Prop.—Gaseous, not hitherto condensed into a liquid; colourless, tasteless, and inodorous; excites violent spasm of the glottis when an attempt is made to inhale it; sp. gr. = 1·0377, and 100 C. I. weigh 32·137 grains. Water at 60° dissolves about 11 per cent. It has no action on test paper; but if any free oxygen is present, it produces dense, suffocating, acid vapours of a red or orange colour, called *nitrous acid vapours*, which are freely absorbed by water, and render it acid. This character distinguishes it from all other gases, and is a good test of the presence of free oxygen. In some cases it supports combustion: burning sulphur and a lighted candle are extinguished by it; but charcoal and phosphorus, when in vivid combustion, burn in it with increased brilliancy. The product of the combustion is carbonic acid in the former case, and metaphosphoric acid in the latter, nitrogen being separated in both instances. With an equal bulk of hydrogen it forms a mixture which cannot be made to explode, but which is kindled by contact with a lighted candle, and burns rapidly with a greenish white flame, water and pure nitrogen gas being the sole products. The action of freshly ignited spongy platinum on a mixture of hydrogen and binoxide of nitrogen gases leads to the slow production of water and ammonia.

It is partially resolved into its elements by being passed through red-hot tubes, and a succession of electric sparks has a similar effect. It is converted into protoxide of nitrogen by substances which have a strong affinity for oxygen, such as moist iron filings, and a solution of sulphuret of potassium. Davy ascertained its composition by the combustion of charcoal (Elements of Chemical Philosophy, p. 200). Two volumes of the binoxide yielded one volume of nitrogen, and about one of carbonic acid; whence it was inferred to consist of equal measures of oxygen and nitrogen gases united without any condensation. Gay-Lussac (Mémoires d'Arcueil) proved that this proportion is rigidly exact. He decomposed 100 measures of the gas, by heating potassium in it; when 50 measures of pure nitrogen were left, and the potassa formed corresponded to 50 measures of oxygen. The same fact has been lately proved by Henry (An. of Phil. N. S. viii. 299). Hence, as

50 cubic inches of oxygen gas weigh . . .	17·054 grains
50 do. nitrogen	15·083
100 cubic inches of the binoxide must weigh . .	32·137

From the invariable formation of red-coloured acid vapours, whenever binoxide of nitrogen and oxygen are mixed together, these gases detect the presence of each other with great certainty; and since the product is wholly absorbed by water, either of them may be entirely removed from any gaseous mixture by adding a sufficient quantity of the other. Priestley, who first observed this fact, supposed that combination takes place between them in one proportion only; and inferring on this supposition, that a given absorption must always indicate the same quantity of oxygen, he was led to employ binoxide of nitrogen in Eudiometry. But in this opinion he was mistaken. The discordant results obtained by his method soon excited suspicion of their accuracy; and the source of error has since been discovered by the researches of Dalton and Gay-Lussac. It appears from the experiments of Gay-Lussac, and his results do not differ materially from those of Dalton, that for 100 measures of oxygen, 400 of the binoxide may be absorbed as a maximum, and 133 as a minimum; and that between these extremes, the quantity of the binoxide corresponding to 100 of oxygen is exceedingly variable. It does not follow from this, that oxygen and binoxide of nitrogen unite in every proportion within these limits. The true explanation is, that the mixture of these gases may give rise to three compounds,—hyponitrous, nitrous, and nitric acids; and that either may be formed almost, if not entirely, to the exclusion of the others, if certain precautions are adopted. But in the usual mode of operating, two if not all are generated at the same time, and in a proportion to each other which is by no means uniform. The circumstances that influence the degree of absorption, when a mixture of oxygen and binoxide of nitrogen is made over water, are the following:—1. The diameter of the tube; 2. The rapidity with which the mixture is made; 3. The relative proportion of the two gases; 4. The time allowed to elapse after mixing them; 5. Agitation of the tube; and lastly, The opposite conditions of adding the oxygen to the binoxide, or the binoxide to the oxygen.

The binoxide may, notwithstanding, be usefully employed in Eudiometry. Dalton operates (An. of Phil. x. 38, and Henry's Elements) by mixing the gases in a graduated tube about ½ an inch wide over water, and waiting, without agitating the mixture, till decrease of volume is at an end, which usually occurs in less than 6 or 10 minutes. Every 27 measures which have disappeared, indicate 10 of oxygen. A large excess of the binoxide should be avoided; and if the gas under examination contain more than 20 per cent. of oxygen, it should be previously diluted with nitrogen. Gay-Lussac advises that 100 measures of the gas under examination should be introduced into a very wide tube or jar, and that an equal volume of the binoxide should then be added (Mém. d'Arcueil, ii. 247). The red vapours, which are instantly produced, disappear very quickly; and the absorption, after half a minute, or a minute at the most, may be regarded as complete. The residue is then transferred into a graduated tube and measured. One-fourth of the loss is oxygen.—Results very near the truth may be obtained by both methods.

If a current of the binoxide be conducted into a solution of protosulphate of iron, the gas is absorbed in large quantity, and the solution acquires a deep olive-brown colour, which appears almost black when fully saturated. This solution absorbs oxygen with facility. But it cannot be safely employed in Eudiometry; because the absorption of oxygen is accompanied, or at least very soon followed, by evolution of gas from the liquid itself. The binoxide is combined with the sulphate in the ratio of 1 eq. of the former to 4 eq. of the latter; and the gas may be recovered by exposure to a vacuum, the original salt being left unchanged (Péligot in An. de Ch. et Ph. liv. 17). On applying heat, part of the gas is evolved and part decomposed: the protoxide of iron takes oxygen both from the binoxide and from water, forming peroxide of iron; while the hydrogen of the decomposed water, and nitrogen of the binoxide combine together, and generate ammonia. Nitric acid is formed when the solution is exposed to the air or oxygen gas, but not otherwise (Davy). When a mixture of binoxide of nitrogen and sulphurous acid are brought into contact with a solution of potassa or ammonia, both gases are absorbed, and a peculiar acid is generated, which has been called by Pelouze, its discoverer, *nitrosulphuric acid.* It is composed of 1 eq. of nitrogen, 1 of sulphur, and 4 of oxygen, 200 volumes of binoxide of nitrogen combining with 100 of sulphurous acid. The nitrosulphates are very prone to decomposition, a sulphate being formed with the evolution of protoxide of nitrogen: this ensues by the mere contact of certain substances, which do not themselves undergo any change, such as spongy platinum, silver and its oxide, charcoal powder, peroxide of manganese, and solutions of corrosive sublimate, lunar caustic, and the sulphates of the oxides of zinc, copper, and iron. The same effect is produced by an acid, as when an attempt is made to procure nitrosulphuric acid in a separate state, even the carbonic acid of the atmosphere being capable of causing the decomposition. The crystals of the nitrosulphates of potash and ammonia may be preserved in well-stopped bottles at ordinary temperatures; the solutions, on the contrary, are not stable above the freezing point, but the stability is much increased by an excess of alkali. On this is founded the best mode of preparing the nitrosulphates, which consists in transmitting binoxide of nitrogen through a strong solution of sulphite of ammonia or potash with an excess of alkali, when the corresponding nitrosulphate separates in colourless prismatic or acicular crystals. The dry crystals decompose at a moderate heat, namely, at 230° for the ammoniacal salt, and 266° for that of potash, the former giving rise to a slight explosion owing to the rapid evolution of protoxide of nitrogen. The decomposition of the nitrosulphate of potassa by heat is particularly interesting, from its forming sulphite of potassa and binoxide of nitrogen instead of sulphate of potassa and the protoxide, as occurs in every other instance. (Lieb. Ann. xv. 240.)

It is singular that both binoxide and protoxide of nitrogen, notwithstanding the absence of acidity, are capable of forming compounds of considerable permanence with the pure alkalies. The circumstances which give rise to the formation of these compounds will be stated in the description of nitre.

Its eq. is = 30·15; eq. vol. = 200; symb. $N + 2O$, NO_2, or $\ddot{N}$.

HYPONITROUS ACID.

Hist. and Prep.—First prepared by Gay-Lussac, who showed that on adding binoxide of nitrogen in excess to oxygen gas, confined in a glass tube over mercury, the absorption is always uniform, provided a strong solution of pure potassa is put into the tube before mixing the two gases: 50 measures of oxygen gas combine under these circumstances with 200 of the binoxide, forming an acid which unites with the potassa. As the binoxide contains half its volume of oxygen gas, the new acid must be composed of 100 measures of nitrogen and 150 of oxygen, as already stated. It is generated when the binoxide is kept for a considerable time, say three months, in a glass tube over mercury, with a strong solution of pure potassa, when the binoxide is resolved into hyponitrous acid, which unites with the alkali, while protoxide of nitrogen remains in the tube; and Dulong formed it by mixing 200 measures of binoxide of nitrogen with 50 of oxygen gas, both quite dry, and exposing the resulting orange fumes to intense cold, which condensed it into a liquid. It is the *nitrous* acid of Berzelius and other Continental chemists.

Prop.—At 0° it is a colourless liquid, and green at common temperatures. It is so volatile, that in open vessels the green fluid wholly and rapidly passes off in the form of an orange vapour, which is said by Mitscherlich to have a density of 1·72. On admixture with water it is converted into nitric acid and binoxide of nitrogen, the latter escaping with effervescence; but when much nitric acid is present, the hyponitrous is changed into nitrous acid, the presence of which imparts several shades of colour, orange, yellow, green, and blue, according as its quantity is more or less predominant. One eq. of hyponitrous and one of nitric acid yield two eq. of nitrous acid:—Thus NO_3 and NO_5 obviously contain the elements for forming $2NO_4$.

Hyponitrous acid does not unite directly with alkalies, being then resolved principally into nitric acid and binoxide of nitrogen; but the hyponitrites of the alkalies and alkaline earths may be obtained by heating the corresponding nitrates to a gentle red heat;

and the hyponitrite of the oxide of lead is formed by boiling a solution of the nitrate of that oxide with metallic lead.

Hyponitrous acid forms with water and sulphuric acid a crystalline compound, which is formed in large quantity during the manufacture of sulphuric acid, and the production of which is an essential part of that process. It is generated whenever moist sulphurous acid gas and nitrous acid vapour are intermixed, being instantly deposited in the form of white acicular crystals; and Gay-Lussac discovered that it may also be made by the direct action of anhydrous nitrous and strong sulphuric acid. The first attempt to determine its composition analytically was by Henry, who found it to consist of 1 eq. of hyponitrous acid, 5 of sulphuric acid, and 5 of water. (Ann. of Phil. xxvii. 367.) G. De Claubry has lately repeated the analysis of the same compound in a state of more perfect dryness, and by what he considers a better method; and he gives as its constituents 2 eq. of hyponitrous acid, 4 of water, and 5 of sulphuric acid. (An. de Ch. et Ph. xlv. 284.) The theory of its production has been very carefully studied by De Claubry. It appears that when moist sulphurous and nitrous acids react on each other, the former is converted into sulphuric and the latter into hyponitrous acid, the oxygen lost by one being gained by the other, $NO_4 + SO_2 = NO_3 + SO_3$. A little nitrogen gas is always disengaged at the same time, which can only arise from a small portion of nitrous acid losing the whole of its oxygen. The action of sulphuric on nitrous acid is different: in this case the nitrous acid is resolved into nitric and hyponitrous acids, $2NO_4 = NO_5 + NO_3$, the latter uniting with sulphuric acid and most of its water to produce the crystalline solid, while the remainder of the water unites with the nitric acid. When the crystalline matter is put into water, the hyponitrous is resolved into nitrous acid and binoxide of nitrogen, both of which escape with effervescence, $2NO_3 = NO_4 + NO_2$. If much water is present, more or less of the nitrous acid is converted into nitric acid and the binoxide. Similar changes ensue when the crystalline are exposed to the air, humidity being rapidly absorbed. This subject has also been examined by Bussy with similar results.

Its eq. is $= 38·15$; symb. $N + 3O$, NO_3, or $\dddot{N}$.

NITROUS ACID.

Prep.—It is always formed when binoxide of nitrogen and oxygen gases are intermixed. Davy showed, by making the mixture in a dry glass vessel previously exhausted, that nitrous acid vapour is formed by the action of 200 measures of the binoxide on 100 of oxygen gas; and hence, as 200 of the binoxide contains 100 of nitrogen and 100 of oxygen, nitrous acid was inferred to consist of 100 measures of nitrogen united with 200 of oxygen gas (page 205). This inference has been confirmed by the researches of Gay-Lussac and Dulong (An. de Ch. et Ph. i. and ii.), the former of whom also proved that its elements contract to 1-3rd of their volume, or in other words, 100 measures of nitrous acid vapour contain 100 of nitrogen gas and 200 of oxygen. The specific gravity of this vapour ought to be 3·1777, formed of 0·9727 the sp. gr. of nitrogen + 2·2050 twice the sp. gr. of oxygen. It is best prepared by heating to redness in an earthen retort the nitrate of oxide of lead, carefully dried; when nitric acid is resolved into nitrous acid and oxygen, and on receiving the products in a dry tube, surrounded by a mixture of ice and salt, the former is condensed. The following equation represents the decomposition:—

$$PbO, NO_5 = PbO + O + NO_4.$$

Prop.—An anhydrous liquid of sp. gr. 1·451, and orange colour at 60°, yellow at 32°, and almost colourless at 0°; acid, pungent, and powerfully corrosive; and imparts a yellow stain to the skin. It is very volatile, boiling at 82°: in a stopped bottle it preserves its liquid form at 60°; but when exposed to the atmosphere it is rapidly dissipated in orange red fumes, which when once mixed with air or other gases require intense cold for condensation.

Nitrous acid vapour is characterized by its orange red colour, acid reaction, and by being absorbed by water with disengagement of binoxide of nitrogen and formation of nitric acid. It is quite irrespirable, exciting great irritation and spasm of the glottis, even when moderately diluted with air. A taper burns in it with considerable brilliancy. It extinguishes burning sulphur; but the combustion of phosphorus continues in it with great vividness.

Nitrous acid is a powerful oxidizing agent, readily giving oxygen to the more oxidable metals, and to most substances which have a strong affinity for it. The acid is decomposed at the same time, being commonly changed into binoxide of nitrogen, though sometimes the protoxide and even pure nitrogen gases are evolved. When transmitted through a red-hot porcelain tube it suffers decomposition, and a mixture of oxygen and nitrogen gases is obtained.

When nitrous acid is mixed with a considerable quantity of water, it is instantly resolved into nitric acid, which unites with the water, and binoxide of nitrogen which escapes with effervescence. Three eq. of nitrous acid yield two eq. of nitric acid and one of the binoxide; for $3NO_4 = 2NO_5 + NO_2$. When a rather small quantity of water is used, the evolved binoxide, at first considerable, becomes less and less as successive quantities of nitrous acid are added, till at last the evolution of gas ceases altogether. The colour of the solution varies remarkably during the process: from being colourless, the liquid acquires a blue tint, then passes into bluish green, green, yellow, and lastly orange. These different solutions contain different relative quantities of nitric acid, nitrous acid, and water, on which circumstance the varying shades of colour depend. Nitric and nitrous acids are disposed to unite with each other, and the influence of this attraction enables nitrous acid to sustain admixture with water without decomposition. Strong nitric acid will unite with a considerable quantity of nitrous acid, and thereby acquires an orange red tint. In a weaker nitric acid the water decomposes part of the nitrous acid, and the colour of the solution is orange or yellow. As the strength of the nitric acid becomes weaker and weaker, the quantity of nitrous acid which it can protect from decomposition becomes less and less, and the colour of the solution varies from yellow to green and blue, and is at length colourless. These changes may be witnessed, not only by adding successive quantities of nitrous acid to water, and thereby at length producing a strong nitric acid, but commencing with the latter, saturating it with nitrous acid, and then successively diluting with water.

When nitrous acid is mixed with a very small quantity of water, no binoxide of nitrogen is disengaged, but the liquid becomes green, like the colour of hyponitrous acid. I have repeatedly obtained a similar liquid in preparing nitrous acid from nitrate of oxide of lead, when the materials were not adequately dried; and that green liquid, when allowed to dissipate in the air, leaves some nitric acid behind. From these facts it seems probable that in the decomposition of nitrous acid by water, the first change is the conversion of nitrous into nitric and hyponitrous acids, which last is subsequently changed, when the required quantity of water is present, into nitric acid and binoxide of nitrogen. It may thus well happen that hyponitrous acid contributes to produce the varying colours above described.

Some chemists consider nitrous acid as a compound of nitric and hyponitrous acids, rather than of nitrogen and oxygen. In fact, on adding nitrous acid to an alkaline solution, we obtain a nitrate and hyponitrite; a circumstance which has given rise to the notion that nitrous acid cannot act as a distinct acid.

Its eq. is 46·15; eq. vol. = 100; symb. $N + 4O$, NO_4, or $\overset{....}{N}$.

NITRIC ACID.

Hist.—If a succession of electric sparks be passed through a mixture of oxygen and nitrogen gases confined in a glass tube over mercury, a little water being present, the volume of the gases will gradually diminish, and the water after a time will be found to have acquired acid properties. On neutralizing the solution with potassa, or what is better, by putting a solution of that alkali instead of water into the tube at the beginning of the experiment, a salt is obtained which possesses all the properties of nitrate of potassa. This experiment was performed in 1785 by Cavendish, who inferred from it that nitric acid is composed of oxygen and nitrogen, though the acid itself, under the name of *spirit of nitre*, had been long previously known. The best proportion of the gases was found to be seven of oxygen to three of nitrogen; but as some nitrous acid is always formed during the process, the exact composition of nitric acid cannot in this way be accurately determined.

Nitric acid may be formed much more conveniently by adding binoxide of nitrogen slowly over water to an excess of oxygen gas. Gay-Lussac proved that nitric acid may in this manner be obtained quite free from nitrous or hyponitrous acid; and that it is composed of 100 measures of nitrogen and 250 of oxygen, a result fully confirmed by Davy, Henry, Berzelius, and others.

Nitric acid cannot exist in an insulated state. Binoxide of nitrogen and oxygen gases never form nitric acid if mixed together when quite dry; and nitrous acid vapour may be kept in contact with oxygen gas without change, provided no water is present. The most simple form under which chemists have hitherto procured nitric acid is in solution with water; a liquid which, in its concentrated state, is the nitric acid of the pharmacopœia. By manufacturers it is better known by the name of *aqua fortis*.

The nitric acid of commerce is procured by decomposing some salt of nitric acid by means of oil of vitriol, and common nitre, as the cheapest of the nitrates, is employed for the purpose. This salt, previously well dried, is put into a glass retort, and a quantity of the strongest oil of vitriol is poured upon it. On applying heat, ebullition ensues, owing to the escape of nitric acid vapours, which must be collected in a receiver kept cold by moist cloths. The heat should be steadily increased during the operation, and continued as long as any acid vapours come over.

Chemists differ as to the best proportions for forming nitric acid. The London College recommends equal weights of nitre and oil of vitriol; and the Edinburgh and Dublin Colleges employ three parts of nitre to two of the acid. In the process of the London College the alkali of the nitre is left as a bisulphate in the retort; since one eq. of nitre (54 nitric acid and 47 potassa) is 100, and the nearly equal number 98 corresponds to 2 eq. of oil of vitriol, which contain 2 eq. of anhydrous sulphuric acid and 2 eq. of water. During the distillation the nitric acid passes over along with 1 eq. of water, and 1 eq. of water is retained by the bisulphate of potassa. The reaction may be thus expressed:—

$$KO, NO_5 + 2\,(HO, SO_3) = HO, NO_5 + (KO, HO, 2SO_3).$$

The presence of water is essential: nitric acid of 1·50 consists of real or anhydrous acid and water in the ratio of 1 eq. of each, and unless water in at least this proportion be supplied, a proportional quantity of nitric acid is resolved, at the moment of quitting the potassa, into oxygen and nitrous acid (Phillips, in Phil. Mag. ii. 430). If the mixture be introduced into the retort without soiling its neck, and the heat be cautiously raised, the product will be quite free from sulphuric acid; and therefore the second distillation from nitre, recommended in the pharmacopœia, is superfluous.

The proportions of the Edinburgh and Dublin Colleges are such, that the residual salt is a mixture of sulphate and bisulphate of potassa. The acid of the nitre does not receive from the oil of vitriol the requisite quantity of water, and hence part of it is decomposed, yielding towards the close of the operation an abundant supply of nitrous acid fumes. If the receiver be kept cool, nearly all these vapours are condensed, and the product is a mixture of nitric and nitrous acids, of a deep orange red colour, very strong and fuming, and of a greater sp. gr. though proportionally less in quantity, than that obtained by the foregoing process. The sp. gr. of the pale acid is 1·500; while that of the red acid is 1·520, or by previously drying the nitre and boiling the sulphuric acid, Hope states that it may be made so high as 1·54.

Some manufacturers decompose nitre with half its weight of sulphuric acid, thus employing the ingredients in the proportion of 1 eq. of each. In this case about half of the nitric acid is decomposed, and considerable loss sustained, unless the requisite quantity of water is previously mixed with the sulphuric acid, or water be placed in the receiver to condense the nitrous acid. Some of the nitre is likewise apt to escape decomposition; and the residue, consisting of neutral sulphate, which is much less soluble than the bisulphate, is removed from the retort with difficulty.

In none of the preceding processes, not even in the first, is the product quite colourless; for at the commencement and close of the operation, nitrous acid fumes are disengaged, which communicate a straw yellow or an orange red tint, according to their quantity. If a very pale acid is required, two receivers should be used; one for condensing the colourless vapours of nitric acid, and another for the coloured products. The coloured acid is called nitrous acid by the College; but it is in reality a mixture or compound of nitric and nitrous acids, similar to what may be obtained by mixing anhydrous nitrous with colourless nitric acid. It is easy to convert the common mixed acid of the College into colourless nitric acid, by exposing the former to a gentle heat for some time, when all the nitrous acid will be expelled. But this process is rarely necessary, as the coloured acid may be substituted in most cases for that which is colourless. Where an acid of great strength is required, the former is even preferable.

Nitric acid frequently contains portions of sulphuric and hydrochloric acid. The former is derived from the acid which is used in the process, and the latter from sea-salt, which is frequently mixed with nitre. These impurities may be detected by adding a few drops of a solution of chloride of barium and oxide of silver to separate portions of nitric acid, diluted with three or four parts of distilled water. If chloride of barium cause a cloudiness or precipitate, sulphuric acid must be present; if a similar effect be produced by nitrate of oxide of silver, the presence of hydrochloric acid may be inferred. Nitric acid is purified from sulphuric acid by redistilling it from a small quantity of nitrate of potassa, with the alkali of which the sulphuric acid unites, and remains in the retort. To separate hydrochloric acid, it is necessary to drop a solution of nitrate of oxide of silver into the nitric acid as long as a precipitate is formed, and draw off the pure acid by distillation.

Prop.—A strong, highly corrosive acid; in its purest and most concentrated state a colourless liquid, of sp. gr. 1·50 or 1·510, chemically combined with water, from which it cannot be separated without decomposition, or by uniting with some other body. An acid of sp. gr. 1·50 contains 25 per cent. of water, according to the experiments of Phillips, and 20·3 per cent. according to those of Ure.* Nitric acid of this strength emits dense, white, suffocating vapours when exposed to the atmosphere. It attracts watery vapour from the air, whereby its density is diminished. A rise of temperature is occasioned by mixing it with a certain quantity of water. When 58 measures of nitric acid of sp. gr. 1·5 are suddenly mixed with 42 of water, the temperature rises from 60° to 140°; and the mixture, on cooling to 60°, occupies the space of 92·65 measures instead of 100. From its strong affinity for water, it occasions snow to liquefy with great rapidity; and if the mixture is made in due proportion, intense cold will be generated. (Page 42.) It boils at 248°, and may be distilled without suffering material change. An acid of lower density than 1·42 becomes stronger by being heated; because the water evaporates more rapidly than the acid. An acid, on the contrary, which is stronger than 1·42 is weakened by the application of heat. It may be frozen by cold: the point of congelation varies with the strength of the acid. The strongest acid freezes at about 50° below zero. When diluted with half its weight of water, it becomes solid at $-1\frac{1}{2}°$; but a little more water lowers its freezing point to $-45°$. It acts powerfully on oxidable substances, and is hence much employed by chemists for bringing bodies to their maximum of oxidation. Nearly all the metals are oxidized by it; and some of them, such as tin, copper, and mercury, are attacked with great violence. If flung on burning charcoal, it increases the brilliancy of its combustion in a high degree. Sulphur and phosphorus are converted into acids by its action. All vegetable substances are decomposed by it. In general the oxygen of the nitric acid enters into direct combination with the hydrogen and carbon of those compounds, forming water with the former, and carbonic acid with the latter. This happens remarkably in those compounds in which hydrogen and carbon are predominant, as in alcohol and the oils. It effects the decomposition of animal matters also. The cuticle and nails receive a permanent yellow stain when touched with it; and if applied to the skin in sufficient quantity it acts as a powerful cautery, destroying the organization of the part entirely.

---

* See his Table in the Appendix, showing the strength of diluted acid of different densities.

When oxidation is effected through the medium of nitric acid, the acid itself is commonly converted into binoxide of nitrogen. This gas is sometimes given off nearly quite pure; but in general some nitrous acid, protoxide of nitrogen, or pure nitrogen, are evolved at the same time. The escape of nitrous acid in these cases seems owing, according to some late observations of Phillips, not so much to its direct formation, as to the binoxide at first formed acting on the nitric acid of the solution. Direct solar light deoxidizes nitric acid, resolving a portion of it into oxygen and nitrous acid. The former escapes as gas; the latter is absorbed by the nitric acid, and converts it into the mixed nitrous acid of the shops. When the vapour of nitric acid is transmitted through red-hot porcelain tubes, it suffers complete decomposition, and a mixture of oxygen and nitrogen gases is the product.

Nitric acid may also be deoxidized by transmitting a current of binoxide of nitrogen through it. That gas, by taking oxygen from the nitric, is converted into nitrous acid; and a portion of nitric acid, by losing oxygen, passes into the same compound. The nitrous acid, thus derived from two sources, gives a colour to the nitric acid, the depth and kind of which depend on the strength of the acid. On saturating with binoxide of nitrogen four separate portions of nitric acid of sp. gr. 1·15, 1·35, 1·40, and 1·50, the colour will be blue in the first, green in the second, yellow in the third, and brownish red in the fourth; and acid of 1·05 is not coloured at all. Phillips found that acid of density 1·497 acquired a density 1·541, that is, was made stronger, by saturation with the binoxide; but those acids which become green are much weakened, because nitrous acid vapour is mechanically carried off by those portions of binoxide which pass unabsorbed through the liquid.

Tests.—All the salts of nitric acid are soluble in water, and therefore it is impossible to precipitate that acid by any reagent. The presence of nitric acid, when uncombined, is readily detected by its strong action on copper and mercury, emitting ruddy fumes of nitrous acid, and by its forming with potassa a neutral salt, which crystallizes in prisms, and has all the properties of nitre.

Gold leaf is a still more delicate test. When hydrochloric acid is added to the solution of a nitrate, chlorine is disengaged, and the liquid hence acquires the property of dissolving gold leaf; but as the action of hydrochloric acid on the salts of chloric, bromic, iodic, and selenic acids likewise yields a solution capable of dissolving gold, no inference can be drawn from the experiment, unless the absence of these acids shall have been previously demonstrated. Another character which may be useful is to mix the supposed nitric acid or nitrate with dilute sulphuric acid in a tube, add a few fragments of pure zinc, and set fire to the hydrogen as it issues: if nitric acid be present, the flame of the hydrogen will have a greenish white tint, due to admixture with binoxide of nitrogen. This test occurred to my assistant, Mr. Balmain; and Mr. Maitland at the same time proposed alcohol instead of zinc with the same intention. A very delicate test has been proposed by O'Shaugnessy, founded on the orange red followed by a yellow colour, which nitric acid communicates to morphia. The supposed nitrate is heated in a test tube with a drop of sulphuric acid, and then a crystal of morphia is added. (Lancet, 1829-30.) It is advisable to try the process in a separate tube with the sulphuric acid alone, in order to prove the absence of nitric acid. But the most delicate test is the following, proposed by Derbanius de Richemont:—The suspected substance is mixed with pure sulphuric acid in a tube, and gently warmed, and a solution of green vitriol cautiously added. At the line of junction of the two liquids, the dark colour produced by the action of nitric acid on the protosulphate of iron is distinctly seen, even when only $\frac{1}{24000}$ of nitric acid is present.

SECTION VI.

CARBON.

Hist. and Prep.—It occurs pure and crystallized in forms of the octohedral system in the diamond, a mineral of unknown origin, but probably derived from the slow decomposition of vegetable matter. It is sometimes a constituent of the rocks in the form of small tabular crystals called graphite, and in larger masses mixed with iron, as plumbago with which pencils are made, and in anthracite mixed with earth and metallic sulphurets. It is the essential principle of the different varieties of charcoal—the black mass left when most vegetable and animal matters are heated to redness in close vessels, and which contains any fixed principles originally present in its source. Common charcoal is made from wood and contains about 1-50th of its weight of alkaline and earthy salts, which constitute the ashes when wood-charcoal is burned. Coke is the charcoal from coal, ivory black or animal charcoal is that from bones, lamp-black from resin. Very pure varieties of charcoal may be formed from spirit of wine, turpentine, sugar, and starch.

Prop.—Carbon, as it exists in the diamond, is the hardest substance in nature ; sp. gr. 3·52 ; it crystallizes in the regular system in forms which are frequently hemihedral, and are characterized by a perfect cleavage parallel to the faces of the octohedron ; beautifully transparent and a powerful refractor of light ; a non-conductor of heat and electricity. It is very unchangeable, resists the action of acids and alkalies, and bears the most intense heat in close vessels without fusing or undergoing any perceptible change. Heated to redness in the open air, it is entirely consumed. Newton first suspected it to be combustible from its great refracting power, a conjecture which was rendered probable by the experiments of the Florentine academicians in 1694. Lavoisier first proved it to contain carbon by throwing the sun's rays, concentrated by a powerful lens, upon a diamond contained in a vessel of oxygen gas. The diamond was consumed entirely, oxygen disappeared, and carbonic acid was generated. It has since been demonstrated by the researches of Guyton-Morveau, Smithson Tennant, Allen and Pepys, and Davy, that carbonic acid is the product of its combustion. Guyton-Morveau inferred from his experiments that the diamond is pure carbon, and that charcoal is an oxide of carbon. Tennant burned diamonds by heating them with nitre in a gold tube ; and comparing his own results with those of Lavoisier on the combustion of charcoal, he concluded that equal weights of diamond and pure charcoal, in combining with oxygen, yield precisely equal quantities of carbonic acid. He was thus induced to adopt the opinion, that charcoal and the diamond are chemically the same substance ; and that the difference in their physical character is solely dependent on a difference of aggregation.* This conclusion was confirmed by the experiments of Allen and Pepys †, and Davy ‡, who compared the product of the combustion of the diamond with that derived from different kinds of charcoal. The latter chemist did indeed observe the production of a minute quantity of water during the combustion of the purest charcoal, indicative of a trace of hydrogen; but its quantity is so small, that it cannot be regarded as a necessary constituent. It proves only that a trace of hydrogen is retained by charcoal with such force, that it cannot be expelled by the temperature of ignition.

---

* Phil. Trans. 1797.

† Ibid. 1807.

‡ Ibid. 1814.

Charcoal, as obtained from wood, is hard and brittle, conducts heat very slowly, but is a good conductor of electricity; quite insoluble in water, is attacked with difficulty by nitric acid, and is little affected by any of the other acids, or by the alkalies. It undergoes little change from exposure to air and moisture, being less injured under these circumstances than wood. It is exceedingly refractory in the fire, if excluded from the air, supporting the most intense heat which chemists are able to produce without change.

It possesses the property of absorbing a large quantity of air or other gases at common temperatures, and of yielding the greater part of them again when it is heated. It appears from the researches of Saussure, that different gases are absorbed by it in different proportions. His experiments were performed by plunging a piece of red-hot charcoal under mercury, and introducing it when cool into the gas to be absorbed. He found that charcoal prepared from box-wood absorbs, during the space of 24 or 36 hours, of

Ammoniacal gas . . .	90 times its volume.
Muriatic acid . . .	85
Sulphurous acid . . .	65
Sulphuretted hydrogen . .	81 (Dr. C. Henry.)
Nitrous oxide . . .	40
Carbonic acid . . .	35
Olefiant gas . . .	35
Carbonic oxide . . .	9·42
Oxygen	9·25
Nitrogen . . .	7·5
Hydrogen . . .	1·75

The absorbing power of charcoal, with respect to gases, cannot be attributed to chemical action; for the quantity of each gas which is absorbed bears no relation whatever to its affinity for charcoal. The effect is in reality owing to the peculiar porous texture of that substance, which enables it, in common with most spongy bodies, to absorb more or less of all gases, vapours, and liquids with which it is in contact. This property is most remarkable in charcoal prepared from wood, especially in the compact varieties of it, the pores of which are numerous and small. It is materially diminished by reducing the charcoal to powder; and in plumbago, which has not the requisite degree of porosity, it is wanting altogether.

The porous texture of charcoal accounts for the general fact of absorption only; its power of absorbing more of one gas than of another, must be explained on a different principle. This effect, though modified to all appearance by the influence of chemical attraction, seems to depend chiefly on the natural elasticity of the gases. Those which possess such a great degree of elasticity as to have hitherto resisted all attempts to condense them into liquids, are absorbed in the smallest proportion; while those that admit of being converted into liquids by compression, are absorbed more freely. For this reason, charcoal absorbs vapours more easily than gases, and liquids than either.

Allen and Pepys determined experimentally the increase in weight experienced by different kinds of charcoal, recently ignited, after a week's exposure to the atmosphere. The charcoal from fir gained 13 per cent.; that from *lignum vitæ*, 9·6; that from box, 14; from beech, 16·3; from oak, 16·5; and from mahogany, 18. The absorption is most rapid during the first 24 hours. The substance absorbed is both water and atmospheric air, which the charcoal retains with such force, that it cannot be completely separated from them without exposure to a red heat. Vogel has observed that charcoal absorbs oxygen in a much greater proportion from the air than nitrogen. Thus, when recently ignited charcoal, cooled under mercury, was put into a jar of atmospheric air, the residue contained only 8 per cent. of oxygen gas; and if red-hot charcoal be plunged into water, and then introduced into a vessel of air, the oxygen disappears almost entirely. It is said that pure nitrogen may be obtained in this way. (Schweigger's Journal, iv.)

Charcoal likewise absorbs the odoriferous and colouring principles of most animal and vegetable substances. When coloured infusions of this kind are digested with a due quantity of charcoal, a solution is obtained, which is nearly if not quite colourless. Tainted flesh may be deprived of its odour by this means, and foul water be purified by filtration through charcoal. The substance commonly employed to decolorize fluids is animal charcoal reduced to a fine powder. It loses the property of absorbing colouring matters by use, but recovers it by being heated to redness.

Charcoal is highly combustible. When strongly heated in the open air, it takes fire, and burns slowly. In oxygen gas, its combustion is lively, and accompanied with the emission of sparks. In both cases it is consumed without flame, smoke, or residue, if quite pure; and carbonic acid gas is the product of its combustion.

Its eq. is = 6·12; its vapour (theoretical, p. 173) has a sp. gr. = 0·4215, and eq. vol. = 100, and 100 C. I. weigh 13·153 grains.

The composition of the compounds of carbon described in this section is as follows:—

	Carbon.		Oxygen.		Equiv.	Formulæ.
Carbonic Oxide	6·12 or 1 eq.	+	8 or 1 eq.	=	14·12	$C+O$ or CO.
Carbonic Acid	6·12 or 1 eq.	+	16 or 2 eq.	=	22·12	$C+2O$ or CO_2.

Carbonic oxide gas is theoretically considered as a compound of 100 measures of the vapour of carbon and 50 of oxygen condensed into 100 measures; and carbonic acid gas, of 100 measures of the vapour of carbon and 100 of oxygen condensed into 100 measures.

CARBONIC ACID.

Hist.—Discovered by Black in 1757, and described by him in his inaugural dissertation on magnesia under the name of *fixed air.* He observed the existence of this gas in common limestone and magnesia, and found that it may be expelled from these substances by the action of heat or acids. He also remarked that the same gas is formed during respiration, fermentation, and combustion. Its composition was first demonstrated synthetically by Lavoisier, who burned carbon in oxygen gas, and obtained carbonic acid as the product. The same experiment has been repeated by Davy, Allen, and Pepys, and others, with the result that in the combustion of diamond or other pure carbonaceous matter the oxygen undergoes no change of volume, or in other words, that carbonic acid gas contains its own volume of oxygen: hence the difference of the sp. gravities of carbonic acid and oxygen gases (1·524 − 1·1025), or 0·4215, gives the exact ratio of the quantities of carbon and oxygen combined, being 0·4215 to 1·1025, or 6·12 to 16. Smithson Tennant illustrated its nature analytically by passing the vapour of phosphorus over chalk, or carbonate of lime, heated to redness in a glass tube. The phosphorus took oxygen from the carbonic acid, charcoal in the form of a light black powder was deposited, and the phosphoric acid, which was formed, united with the lime.

Prep.—Conveniently by the action of hydrochloric acid, diluted with two or three times its weight of water, on fragments of marble, when carbonic acid gas escapes with effervescence, and chloride of calcium is left in solution.

Prop.—Commonly a colourless gas of a pungent odour and acidulous taste, condensable at 32° by a pressure of 36 atmospheres into a liquid, which congeals by the cold produced by its own evaporation, estimated at − 180°, and at that temperature is solid under the atmospheric pressure, being the first instance of a solidified gas. The sp. gr. of the gas is 1·524, and 100 C. I. at 60° and 30 Bar. weigh 47·262 grains; the sp. gr. of the liquid at 32° is 0·83; it dilates remarkably from heat, its expansion being upwards of four times that of air, 20 volumes of the liquid at 32° occupying 29 volumes at 86°, and its sp. gr. varies from 0·9 to 0·6 as the temperature rises from − 4° to + 86°. When heated from 32° to 86° its elasticity rises from 36 to 73 atmospheres, being 0·68 atmospheres for each degree. It is insoluble in water and fat oils, but soluble in all proportions in ether, alcohol, naphtha, oil of turpentine, and bisulphuret of carbon. The evaporation of its ethereal solution causes an intense degree of cold, by which large quantities of mercury may be frozen. (Thilorier in Ann. de Ch. et Ph. lx. 427.)

Carbonic acid gas extinguishes burning substances of all kinds, and the combustion does not cease from the want of oxygen only. It exerts a positive influence in checking combustion, as appears from the fact, that a candle cannot burn in a gaseous mixture composed of four measures of atmospheric air, and one of carbonic acid.

It is not better qualified to support the respiration of animals; for its presence, even in moderate proportion, is soon fatal. An animal cannot live in air which contains sufficient carbonic acid for extinguishing a lighted candle; and hence the practical rule of letting down a burning taper into old wells or pits before any one ventures to descend. If the light is extinguished, the air is certainly impure; and there is generally thought to be no danger, if the candle continues to burn. But some instances have been known of the atmosphere being sufficiently loaded with carbonic acid to produce insensibility, and yet not so impure as to extinguish a burning candle. (Christison on Poisons, 2nd ed. 707.) When an attempt is made to inspire pure carbonic acid, violent spasm of the glottis takes place, which prevents the gas from entering the lungs. If it be so much diluted with air as to admit of its passing the glottis, it then acts as a narcotic poison on the system. It is this gas which has often proved destructive to persons sleeping in a confined room with a pan of burning charcoal.

It is quite incombustible, and cannot be made to unite with an additional portion of oxygen. It is a compound, therefore, in which carbon is in its highest degree of oxidation.

Lime water becomes turbid when brought into contact with carbonic acid. The lime unites with the gas, forming carbonate of lime, which, from its insolubility in water, at first renders the solution milky, and afterwards forms a white flaky precipitate. Hence lime water is not only a valuable test of the presence of carbonic acid, but is frequently used to withdraw it altogether from any gaseous mixture that contains it.

Recently boiled water dissolves its own volume of carbonic acid gas at 60° and 30 Bar.; but it will take up much more if the pressure be increased. The quantity of the gas absorbed is in exact ratio with the compressing force; that is, water dissolves twice its volume when the pressure is doubled, and three times its volume when the pressure is trebled. A saturated solution may be made by transmitting a stream of the gas through a vessel of cold water during the space of half an hour, or still better by the use of a Woulfe's bottle or Nooth's apparatus, so as to aid the absorption by pressure. Water and other liquids which have been charged with carbonic acid under great pressure, lose the greater part of the gas when the pressure is removed. The effervescence which takes place on opening a bottle of ginger beer, cider, or brisk champaign, is owing to the escape of carbonic acid gas. Water, if fully saturated with carbonic acid gas, sparkles when it is poured from one vessel into another. The solution has an agreeably acidulous taste, and gives to litmus paper a red stain which is lost on exposure to the air. On the addition of lime water to it, a cloudiness is produced, which at first disappears, because the carbonate of lime is soluble in excess of carbonic acid; but a permanent precipitate ensues when the free acid is neutralized by an additional quantity of lime water. The water which contains carbonic acid in solution is wholly deprived of the gas by boiling. Removal of pressure from its surface by means of the air-pump has a similar effect.

The agreeable pungency of beer, porter, and ale, is in a great measure owing to the presence of carbonic acid; by the loss of which, on exposure to the air, they become stale. All kinds of spring and well water contain carbonic acid absorbed from the atmosphere, and to which they are partly indebted for their pleasant flavour. Boiled water has an insipid taste from the absence of carbonic acid.

Carbonic acid is always present in the atmosphere, even at the summit of the highest mountains, or at a distance of several thousand feet above the ground. Its presence may be demonstrated by exposing lime water in an open vessel to the air, when its surface will soon be covered with a pellicle, which is carbonate of lime. The origin of the carbonic acid is obvious. Besides being formed abundantly by the combustion of all substances which contain carbon, the respiration of animals is a fruitful source of it, as may be proved by breathing for a few minutes into lime water; and it is also generated in all the spontaneous changes to which dead animal and vegetable matters are subject. The carbonic acid proceeding from such sources is commonly diffused equably through the air; but when any of these processes occur in low confined situations, as at the bottom of old wells, the gas is then apt to accumulate there, and form an atmosphere called *choke damp*, which is fatal to any animals that are placed in it. These accumulations happily never take place, except when there is some local origin for the carbonic acid; as, for example, when it is generated by fermentative processes going on at the surface of the ground, or when it issues directly from the earth, as happens at the Grotto del Cane in Italy, and at Pyrmont in Westphalia. There is no real foundation for the opinion that carbonic acid can separate itself from the great mass of the atmosphere, and accumulate in a low situation merely by the force of gravity. Such a supposition is contrary to the well-known tendency of gases to diffuse themselves equally through each other. It is also contradicted by observation; for many deep pits, which are free from putrefying organic remains, though otherwise favourably situated for such accumulations, contain pure atmospheric air.

Though carbonic acid is the product of many natural operations, chemists have not hitherto noticed any increase in the quantity contained in the atmosphere. The only known process which tends to prevent increase in its proportion, is that of vegetation. Growing plants purify the air by withdrawing carbonic acid, and yielding an equal volume of pure oxygen in return; but whether a full compensation is produced by this cause has not yet been satisfactorily determined.

Carbonic acid is contained in the earth. Many mineral springs, such as those of Tunbridge, Pyrmont, and Carlsbad, are highly charged with it. In combination with lime it forms extensive masses of rock, which geologists have found to occur in all countries, and in every formation.

Carbonic acid unites with alkaline substances, and the salts so constituted are called *carbonates.* Its acid properties are feeble, so that it is unable to neutralize completely the alkaline properties of potassa, soda, and lithia. For the same reason, all the carbonates, without exception, are decomposed by the hydrochloric and all the stronger acids; when carbonic acid is displaced, and escapes in the form of gas.

Its eq. is 22·12; eq. vol. = 100; symb. $C + 2O$, CO_2, or $\ddot{C}$.

CARBONIC OXIDE GAS.

Hist.—Priestley discovered it by igniting chalk in a gun-barrel, and afterwards obtained it by heating a mixture of chalk and iron filings. He supposed it to be hydrogen mixed with carbonic acid. Its real nature was pointed out by Cruickshank (Nicholson's Journal, 4to ed. v.), and about the same time by Clément and Désormes (An. de Chimie, xxxix.).

Prep.—1. By transmitting carbonic acid gas over red-hot fragments of charcoal contained in a tube of iron or porcelain. 2. By igniting alkaline or earthy carbonates with iron filings, charcoal, or some deoxodizing substance. 3. By heating binoxalate of potassa with five or six times its weight of strong oil of vitriol in a retort. Effervescence soon ensues, owing to the escape of gas consisting of equal measures of carbonic acid and carbonic oxide gases; and on absorbing the former by an alkaline solution, the latter is left in a state of perfect purity. To comprehend the theory of the process it is necessary to premise, that oxalic acid is a compound of equal measures of carbonic acid and carbonic oxide, or at least its elements are in the proportion to form these gases; and that it cannot exist unless in combination with water or some other substance. Now the sulphuric acid unites both with the potassa and water of the binoxalate, and the oxalic acid being thus set free, is instantly decomposed. Oxalic acid may be substituted in this process for binoxalate of potassa. The following equation represents the reaction:—

$$KO, HO, 2C_2O_3+2SO_3=KO, HO, 2SO_3+2CO+2CO_2.$$

Prop.—A colourless, inodorous gas; sp. gr. = 0·9727, and 100 C. I. at 60° and 30 Bar. weigh 30·207 grains; has neither acid nor alkaline properties; is sparingly dissolved by water, and does not render lime water turbid. It is inflammable. When a lighted taper is plunged into it, the taper is extinguished; but the gas itself is set on fire, and burns calmly at its surface with a lambent blue flame. The sole product of its combustion, when the gas is quite pure, is carbonic acid; a fact which proves that it does not contain any hydrogen. It cannot support respiration. It acts injuriously on the system; for if diluted with air, and taken into the lungs, it very soon occasions headache and other unpleasant feelings; and when breathed pure, it almost instantly causes profound coma.

A mixture of carbonic oxide and oxygen gases may be made to explode by flame, by a red-hot solid body, or by the electric spark. If mixed together in the ratio of 100 measures of carbonic oxide and rather more than 50 of oxygen, and the mixture is inflamed in Volta's Eudiometer by electricity so as to collect the product of the combustion, the whole of the carbonic oxide, together with 50 measures of oxygen, disappears, and 100 measures of carbonic acid gas occupy their place. From this fact, first ascertained by Berthollet, and since confirmed by subsequent observation, it follows that carbonic oxide contains half as much oxygen, and as much carbon, as carbonic acid. Accordingly its density should be 0·4215 (sp. gr. of carbon vapour) + 0·5512 (half the sp. gr. of oxygen gas) = 0·9727, which is the number found experimentally by Dulong and Berzelius.

The two first processes mentioned for generating carbonic oxide will now be intelligible. The principle of the methods is to bring carbonic acid at a red heat in contact with some substance which has a strong affinity for oxygen. This condition is fulfilled by igniting chalk, or any carbonate which can bear a red heat without decomposition, such as the carbonates of baryta, strontia, soda, potassa, or lithia, with half its weight of iron filings or charcoal. The carbonate is reduced to the caustic state, and its carbonic acid is converted into carbonic oxide by yielding oxygen to the iron or charcoal. When the former is used, oxide of iron is the product; when charcoal is employed, the charcoal itself is oxidized, and yields carbonic oxide. This gas may likewise be generated by heating to redness a mixture of almost any metallic oxide with one-sixth of its weight of charcoal powder. The oxides of zinc, iron, or copper, are the cheapest and most convenient. In all these processes it is essential that the ingredients be quite free from moisture and hydrogen, otherwise some carburetted hydrogen gas would be generated. The product should always be washed with lime water to separate it from carbonic acid.

Henry has ascertained that when a succession of electric sparks is passed through carbonic acid confined over mercury, a portion of that gas is converted into carbonic oxide and oxygen. When a mixture of hydrogen and carbonic acid gases is electrified, a portion of the latter yields one half of its oxygen to the former; water is generated, and carbonic oxide produced. On electrifying a mixture of equal measures of carbonic oxide and protoxide of nitrogen, both gases are decomposed without change of volume, and the residue consists of equal measures of carbonic acid and nitrogen gases. The carbonic oxide should be in very slight excess, in order to ensure the success of the experiment. On this fact is founded Henry's method of analyzing protoxide of nitrogen, and testing its purity, as will be more particularly mentioned in the fourth part of the work.

Its eq. is 14·12; eq. vol. = 100; symb. $C + O$, CO, or C.

SECTION VII.

SULPHUR.

Hist.—It occurs as a mineral production in some parts of the earth, particularly in the neighbourhood of volcanoes, as in Italy and Sicily. It is commonly found in a massive state; but it is sometimes met with crystallized in the form of a right rhombic octohedron. It exists much more abundantly in combination with several metals, such as silver, copper, antimony, lead, and iron. It is procured in large quantity by exposing iron pyrites to a red heat in close vessels.

Prop.—A nearly tasteless, brittle solid; colour greenish yellow; odour when rubbed peculiar; sp. gr. 1·99; non-conductor of electricity and heat. Its point of fusion is 232°; between 232° and 280° it possesses the highest degree of fluidity, is then of an amber colour, and if cast into cylindrical moulds, forms the common roll sulphur of commerce. It begins to thicken near 320°, and acquires a reddish tint; and at temperatures between 428° and 482°, it is so tenacious that the vessel may be inverted without causing it to change its place. From 482° to its boiling point it again becomes liquid, but never to the same extent as when at 248°. When heated to at least 428°, and then poured into water, it becomes a ductile mass, which may be used for taking the impression of seals.

Fused sulphur has a tendency to crystallize in cooling. A crystalline arrangement is perceptible in the centre of common roll sulphur; and by good management regular crystals may be obtained. For this purpose several pounds of sulphur should be melted in an earthen crucible; and when partially cooled, the outer solid crust should be pierced, and the crucible quickly inverted, so that the inner and as yet fluid parts may gradually flow out. On breaking the solid mass, when quite cold, crystals of sulphur will be found in its interior.

Sulphur is very volatile. It begins to rise slowly in vapour, even before it is completely fused. At 550° or 600° it volatilizes rapidly, and condenses again unchanged in close vessels. Common sulphur is purified by this process; and if the sublimation be conducted slowly, the sulphur collects in the receiver in the form of detached crystalline grains, called *flowers of sulphur.* In this state, however, it is not quite pure; for the oxygen of the air within the apparatus combines with a portion of sulphur during the process, and forms sulphurous acid. The acid may be removed by washing the flowers repeatedly with water.

The sp. gr. of sulphur vapour was found by Dumas to lie between 6·51 and 6·617, and by Mitscherlich 6·9 (An. de Ch. et Ph. lv. 8.): its sp. gr. by calculation (page 174) is 6·648. Hence, could the vapour continue as such at 60° and 30 Bar., 100 cubic inches should weigh 206·17 grains.

Sulphur is insoluble in water. It dissolves readily in boiling oil of turpentine. The solution has a reddish brown colour like melted sulphur, and if fully saturated deposits numerous small crystals in cooling. It is also soluble in alcohol, if both substances are brought together in the form of vapour. The sulphur is precipitated from the solution by the addition of water.

Sulphur, like charcoal, retains a portion of hydrogen so obstinately that it cannot be wholly freed from it either by fusion or sublimation. Davy detected its presence by exposing sulphur to the strong heat of a powerful galvanic battery, when some hydrosulphuric acid gas was disengaged. The hydrogen, from its minute quantity, can only be regarded in the light of an accidental impurity, and as in no wise essential to the nature of sulphur.

When sulphur is heated in the open air to 300° or a little higher, it kindles spontaneously, and burns with a faint blue light. In oxygen gas its combustion is far more vivid; the flame is much larger, and of a bluish white colour. Sulphurous acid is the product in both instances;—no sulphuric acid is formed even in oxygen gas unless moisture be present.

Crystals of native sulphur, which have been formed by the condensation of sulphurous vapour, as well as those which are deposited from a solution of sulphur in any menstruum, possess forms which are either identical, or connected by being referable to the same crystalline axes. Such, on the contrary, as are produced by the cooling of fused sulphur in the manner above described, belong to a different system of crystallization. The condition determining the form is temperature: if the crystal be formed below 232°, it belongs to the right prismatic system; if at that point, to the oblique prismatic. This is proved by the influence of temperature on a crystal of either system: a crystal of fusion when first formed is perfectly clear and transparent, but kept at common temperatures, it soon becomes opaque, and presents the appearance of the roll sulphur of commerce: the same change occurs when a native crystal is placed in a solution of a salt which boils at 232°. The opacity is in both cases produced by a new arrangement of the particles of sulphur, by which, without any change in the exterior form, the internal structure of the crystal is altered to correspond to the crystallization peculiar to the temperature.

The eq. of sulphur is 16·1; eq. vol. 16·66; symb. S.

The compounds of sulphur described in this section are composed as follows:—

	Sulphur.	Oxygen.	Equiv.	Formulæ.
Sulphurous acid	16·1 or 1 eq.	+ 16 or 2 eq.	= 32·1	$S + 2O$ or SO_2
Sulphuric acid	16·1 or 1 eq.	+ 24 or 3 eq.	= 40·1	$S + 3O$ or SO_3
Hyposulphurous acid	32·2 or 2 eq.	+ 16 or 2 eq.	= 48·2	$2S + 2O$ or S_2O_2
Hyposulphuric acid	32·2 or 2 eq.	+ 40 or 5 eq.	= 72·2	$2S + 5O$ or S_2O_5

Taking 16·66 as the eq. vol. of the vapour of sulphur, the weight of which is represented by 1·108 (page 174), these compounds, by measure, are thus constituted:—

	Sulp.	Oxy.	Cond. into.	Densities.
Sulphurous acid	16·66	+ 100	100	1·108 + 1·1025 = 2·2105
Sulphuric acid	16·66	+ 150	100	1·108 + 1·6537 = 2·7617
Hyposulphurous acid	33·33	+ 100	unknown.	
Hyposulphuric acid	33·33	+ 250	unknown.	

SULPHUROUS ACID.

Hist. and Prep.—Discovered as a gas by Priestley. It is the sole product of the combustion of sulphur in air or dry oxygen gas, and is freely evolved, mixed with carbonic acid, when chips of wood, straw, cork, oil, or most other organic matters are heated in strong sulphuric acid, which yields oxygen to the carbon and hydrogen of those substances, and is thereby converted into sulphurous acid. Nearly all the metals, with the aid of heat, have a similar effect: one portion of the acid yields oxygen to the metal, and is thus reduced to sulphurous acid; while the metallic oxide, at the moment of its formation, unites with sulphuric acid. A very pure gas may thus be obtained by means of copper or mercury.

Prop.—Commonly gaseous, colourless, of a pungent suffocating odour, being that emitted by burning sulphur; taste, acid; sp. gr. 2·2105, and 100 C.I. at 60° and 30 Bar. weigh 68·691 grains; it is liquid at 45° under the pressure of two atmospheres, and at 0° under that of one atmosphere. The gas extinguishes all burning bodies which are immersed into it, and is not inflammable. It does not support respiration, but causes violent irritation and spasm of the glottis; and even when diluted with air, it excites cough when inspired, and causes a peculiar uneasiness about the chest. Water, at 60° and 30 Bar. dissolves 33 times its volume, the solution having the peculiar odour of the gas, and yielding it unchanged by ebullition. It has considerable bleaching properties: at first it reddens litmus paper, and then slowly bleaches it; but most vegetable colours, as of the rose and violet, are speedily removed by it without being first reddened. The colouring principle is not destroyed, but may be restored by a stronger acid or by an alkali.

Davy proved that sulphurous acid gas contains exactly its own volume of oxygen (Elements, p. 273), and consequently the difference in the weights or sp. gr. of these gases ($2{\cdot}2105 - 1{\cdot}1025 = 1{\cdot}108$) gives the weight of sulphur combined with oxygen. The sulphur and oxygen are thus found to be in the ratio of 1·108 to 1·1025, or 16·1 to 16.

Liquid sulphurous acid is easily obtained by transmitting the dry pure gas through a glass tube surrounded by a freezing mixture of snow and salt. Its sp. gr. is 1·45; it boils at 14°, and from the rapidity of its evaporation causes intense cold; it conducts electricity (Kemp). When exposed to cold in the moist state, a crystalline solid is formed, which contains 20 per cent. of water, and probably consists of 1 eq. of the acid to 14 eq. of water.

Though sulphurous acid cannot be made to burn by the approach of flame, it has a very strong attraction for oxygen, uniting with it under favourable circumstances, and forming sulphuric acid. The presence of moisture is essential to this change. A mixture of sulphurous acid and oxygen gases, if quite dry, may be preserved over mercury for any length of time without chemical action; but if a little water be admitted, the sulphurous acid gradually unites with oxygen, and sulphuric acid is generated. Many of the chemical properties of sulphurous acid are owing to its affinity for oxygen. The solutions of metals which have a weak affinity for oxygen, such as gold, platinum, and mercury, are completely decomposed by it, those substances being precipitated in the metallic form. Nitric acid converts it instantly into sulphuric acid by yielding some of its oxygen. Peroxide of manganese causes a similar change, and is itself converted into protoxide of manganese, which unites with the resulting sulphuric acid.

Sulphurous acid gas may be passed through red-hot tubes without decomposition. Several substances which have a strong affinity for oxygen, such as hydrogen, carbon, and potassium, decompose it at the temperature of ignition.

Sulphurous acid combines with metallic oxides, and forms salts which are called *sulphites*, which are decomposed by sulphuric acid, and then emit the characteristic odour of sulphurous acid.

Its eq. is 32·1; eq. vol. = 100; symb. $S + 2O$, SO_2, or $\ddot{S}$.

SULPHURIC ACID.

Hist. and Prep.—Sulphuric acid, or *oil of vitriol* as it is often called, was discovered by Basil Valentine towards the close of the 15th century. It is procured for the purposes of commerce by two methods. One of these has been long pursued in the manufactory at Nordhausen in Germany, and consists in decomposing sulphate of oxide of iron (green vitriol) by heat. This salt contains 6 eq. of water of crystallization; and when strongly dried by the fire, it crumbles down into a white powder, which, according to Thomson, contains 1 eq. of water. On exposing this dried protosulphate to a red heat, its acid is wholly expelled, the greater part passing over unchanged into the receiver, in combination with the water of the salt. Part of the acid, however, is resolved by the strong heat employed in the distillation into sulphurous acid and oxygen. The former escapes as gas throughout the whole process; the latter only in the middle and latter stages, since, in the beginning of the distillation, it unites with the protoxide of iron. Peroxide of iron is the sole residue.

The acid, as procured by this process, is a dense, oily liquid of a brownish tint. It emits copious white vapours on exposure to the air, and is hence called *fuming sulphuric acid.* Its sp. gr. is 1·896 or 1·90. According to Thomson it consists of 80 parts or 2 eq. of anhydrous acid, and 9 parts or 1 eq. of water. On putting this acid into a glass retort, to which a receiver surrounded by snow is securely adapted, and heating it gently, a transparent colourless vapour passes over, which condenses into a white crystalline solid. This substance is pure anhydrous sulphuric acid. It is tough and elastic; liquefies at 66° and boils at a temperature between 104° and 122°, forming, if no moisture is present, a transparent vapour. Exposed to the air, it unites with watery vapour, and flies off in the form of dense white fumes. The residue of the distillation is no longer fuming, and is in every respect similar to the common acid of commerce.

The other process for forming sulphuric acid, which is practised in Britain and in most parts of the Continent, is by burning sulphur previously mixed with one-eighth of its weight of nitrate of potassa. The mixture is burned in a furnace so contrived that the current of air, which supports the combustion, conducts the gaseous products into a large leaden chamber, the bottom of which is covered to the depth of several inches with water. The nitric acid yields oxygen to a portion of sulphur, and converts it into sulphuric acid, which combines with the potassa of the nitre; while the greater part of the sulphur forms sulphurous acid by uniting with the oxygen of the air. The nitric acid, in losing oxygen, is converted, partly perhaps into nitrous acid, but chiefly into binoxide of nitrogen, which, by mixing with air at the moment of its separation, gives rise to the red nitrous acid vapours. The gaseous substances, present in the leaden chamber, are therefore sulphurous and nitrous acids, atmospheric air, and watery vapour. The explanation of the mode in which these substances react on each other, so as to form sulphuric acid, was suggested by the experiments of Clément and Désormes (An. de Ch. lix.), and Davy (Elements, p. 276). When dry sulphurous acid gas and nitrous acid vapour are mixed together in a glass vessel quite free from moisture, no change ensues; but if a few drops of water be added, in order to fill the space with aqueous vapour, the white crystalline compound, described at page 223, is immediately produced. Clément and Désormes believed it to consist of sulphuric acid, binoxide of nitrogen, and water; and Davy, of sulphurous acid, nitrous acid, and water. But the observation that the same compound may be made with sulphuric and anhydrous nitrous acids, and that when decomposed by water both nitrous acid and binoxide of nitrogen are disengaged, led Gay-Lussac to the opinion which now seems to be fully substantiated by experiment. A consistent account may, therefore, be given of what really takes place within the leaden chambers.—The mutual reaction of humidity, sulphurous acid, and nitrous acid, gives rise to the crystalline compound of sulphuric acid, hyponitrous acid, and water; and when this solid falls into the water of the chamber, it is instantly decomposed, sulphuric acid is dissolved, and nitrous acid and binoxide of nitrogen escape with effervescence. The nitrous acid thus set free, as well as that reproduced by the binoxide uniting with the oxygen of the atmosphere, is again intermixed with sulphurous acid and humidity, and thus gives rise to a second portion of the crystalline solid, which undergoes the same change as the first. A certain portion of nitric acid is usually formed by the action of water on the nitrous acid; but the presence of sulphuric acid in that water tends to prevent the free decomposition of nitrous acid which pure water produces. Nay, when the water becomes pretty strongly acid, the nitric acid at first generated is reduced, by absorbed sulphurous acid, into the hyponitrous, which unites with sulphuric acid, and remains even after concentration: it is the cause of the evolution of binoxide of nitrogen which usually ensues when common oil of vitriol is diluted, the hyponitrous acid being then decomposed by the water (Dana). When the water of the chamber is sufficiently charged with acid, it is drawn off, and concentrated by evaporation. It hence appears that the oxygen, by which the sulphurous is converted into sulphuric acid, is in reality supplied by the air; that the combination is effected, not directly, but through the medium of nitrous acid; and that a small quantity of nitrous acid is sufficient for the production of a large quantity of sulphuric acid. The decomposition of the crystalline solid by water seems owing to the strong affinity of that liquid for sulphuric acid.

Besides hyponitrous acid, as above stated, it contains potassa, and the oxide of lead and sometimes iron, the first derived from the nitre employed in making it, and the two latter from the leaden chamber. To separate them, the acid should be distilled from a glass or platinum retort: the former may be safely used by putting into it some fragments of platinum leaf, which cause the acid to boil freely on applying heat, without danger of breaking the vessel. Arsenious acid, derived from arsenic in the sulphur used in the manufacture, has been lately detected in most of the oil of vitriol made in Germany; and from that source arsenic is introduced into preparations for which such acid is employed, as into phosphorus and hydrochloric acid. The arsenic is discovered by diluting with water and transmitting through the solution hydrosulphuric acid gas, which causes orpiment to be formed. The oil of vitriol may be purified from arsenious acid by adding a little hydrated peroxide of iron before distilling.

Prop.—As obtained by the second process, pure sulphuric acid is a dense, colourless, oily fluid, which boils at 620° F., and has a sp. gr. in its most concentrated form, of 1·847 or a little higher, never exceeding 1·850. Mitscherlich found the density of its vapour to be 3. It is one of the strongest acids with which chemists are acquainted, and when undiluted is powerfully corrosive. It decomposes all animal and vegetable substances by the aid of heat, causing deposition of charcoal and formation of water. It has a strong sour taste, and reddens litmus paper, even though greatly diluted. It unites with alkaline substances, and separates all other acids more or less completely from their combinations with the alkalies.

In a very concentrated state it dissolves small quantities of sulphur, and acquires a blue, green, or brown tint. Tellurium and selenium are also sparingly dissolved, the former causing a crimson, and the latter a green colour. By dilution with water, these substances subside unchanged; but if heat is applied, they are oxidized at the expense of the acid, and sulphurous acid gas is disengaged. Charcoal also appears soluble to a small extent in sulphuric acid, communicating at first a pink, and then a dark reddish brown tint.

It has a very great affinity for water, and unites with it in every proportion. The combination takes place with production of intense heat. When four parts by weight of the acid are suddenly mixed with one of water, the temperature of the mixture rises, according to Ure, to 300°. By its attraction for water it causes the sudden liquefaction of snow; and if mixed with it in due proportion (p. 43), intense cold is generated. It absorbs watery vapour with avidity from the air, and on this account is employed in the process for freezing water by its own evaporation. Its action in destroying the texture of the skin, and in decomposing animal and vegetable substances in general, seems dependent on its affinity for water.

To ascertain the quantity of real acid present in liquid acid of different strengths, dilute a known weight of the acid moderately with water, and, while warm, add pure anhydrous carbonate of soda, until the solution is exactly neutral. Every 53·3 parts of carbonate of soda, required to produce this effect, correspond to 40·1 parts of real sulphuric acid. If minute precision is not desired, the strength of the acid may be estimated by its sp. gr. according to the table of Ure inserted in the Appendix.

Sulphuric acid of commerce freezes at − 15°. Diluted with water so as to have a sp. gr. of 1·78 it congeals even above 32°, and remains in the solid state, according to Keir, till the temperature rises to 45°. When mixed with rather more than its weight of water, its freezing point is lowered to − 36°.

The composition of sulphuric acid as before given is founded on the observation of Gay-Lussac, that when the vapour of sulphuric acid is passed through a small porcelain tube heated to redness, it is resolved into two measures of sulphurous acid gas and one of oxygen. Berzelius has confirmed this conclusion by directly converting a known weight of sulphur into sulphuric acid.

Chemists possess an unerring test of the presence of sulphuric acid. If a solution of chloride of barium is added to a liquid containing sulphuric acid, it causes a white precipitate, sulphate of baryta, which is characterised by its insolubility in acids and alkalies.

Sulphuric acid does not occur free in nature, except occasionally in the neighbourhood of volcanoes. In combination, particularly with lime and baryta, it is very abundant.

Hyposulphurous Acid.—It may be formed either by digesting sulphur in a solution of any sulphite, or by transmitting a current of sulphurous acid into a solution of sulphuret of calcium or strontium. In the former case, the sulphurous acid takes up an additional quantity of sulphur, and a salt of hyposulphurous acid is obtained; and in the latter, the sulphurous acid gives part of its oxygen to the metal, and its remaining oxygen unites with sulphur.

Three equivalents of sulphurous acid and two of sulphuret of calcium contain the elements for forming two eq. of hyposulphite of lime, one eq. of sulphur being deposited. A convenient solution for this purpose is made by boiling 3 parts of slaked lime and one of sulphur with 20 parts of water for one hour, and decanting the clear liquid from the undissolved portions; but when this solution is used, the deposite of sulphur is abundant. Herschel states that hyposulphurous acid may be formed by the action of sulphurous acid on iron filings; but the nature of the change is not well understood.

The salts of hyposulphurous acid were first described by Gay-Lussac (An. de Ch. lxxxv.) under the name of *Sulphuretted Sulphites.* Thomson in his System of Chemistry suggested that the acid of these salts might be regarded as a compound of one equivalent of sulphur and one of oxygen, and proposed for it the name of *hyposulphurous* acid; and the subsequent researches of Herschel (Phil. Journal, i. 8 and 396) accorded so entirely with this opinion, that it was universally adopted. But it appears from the experiments of Rose, that though the ratio of its elements is as 16 to 8, the equivalent of the acid, or the quantity required to neutralize 1 eq. of an alkali, is not 24, but 48; and hence that its smallest molecule must be formed of 2 atoms of sulphur united with 2 atoms of oxygen (Pog. Ann. xxi. 431).

Prop.—It cannot exist permanently in a free state. On decomposing a hyposulphite by any stronger acid, such as the sulphuric or hydrochloric, the hyposulphurous acid, at the moment of quitting the base, resolves itself into sulphurous acid and sulphur. Herschel succeeded in obtaining free hyposulphurous acid, by adding a slight excess of sulphuric acid to a dilute solution of hyposulphite of strontia; but its decomposition very soon took place, even at common temperatures, and was instantly effected by heat. Most of the hyposulphites are soluble in water, and have a bitter taste. The solution precipitates the nitrates of the oxides of silver and mercury black, as sulphuret of the metals; and salts of baryta and oxide of lead are thrown down as white insoluble hyposulphites of those bases. That of baryta is soluble without decomposition in water acidulated with hydrochloric acid. The solution of all the neutral hyposulphites has the peculiar property of dissolving recently precipitated chloride of silver in large quantity, and forming with it a liquid of an exceedingly sweet taste.

Hyposulphuric Acid.—It was discovered in 1819 by Welter and Gay-Lussac (An. de Ch. et Ph. x.), and is formed by transmitting a current of sulphurous acid gas through water containing peroxide of manganese in fine powder; when by a new arrangement of their elements,

2 eq. Sulp. acid & 1 eq. Perox. Mang. yield 1 eq. Protox. Mang. & 1 eq. Hyposulp. acid,
$2SO_2$ MnO_2 MnO S_2O_5

hyposulphate of protoxide of manganese remaining in solution. During the action heat is freely evolved, and in consequence sulphuric acid is also generated; but if the peroxide of manganese be pure and the materials kept cool, the formation of sulphuric acid is almost completely prevented. To the liquid, after filtration, a solution of pure baryta or sulphuret of barium in slight excess is added, whereby the manganese is thrown down as an oxide or sulphuret, sulphuric acid as sulphate of baryta, and a solution of hyposulphate of baryta is obtained: the excess of baryta is got rid of by a free current of carbonic acid gas, and then heating the solution. The hyposulphate of baryta crystallizes by evaporation, and on decomposing a solution of that salt by a quantity of sulphuric acid exactly sufficient for precipitating the baryta, the hyposulphuric acid is left in solution.

Prop.—Taste sour; distinct acid reaction; neutralizes alkalies; inodorous, and thus distinguished from sulphurous acid; forms soluble salts with baryta, strontia, lime, and oxide of lead, by which it is distinguished from sulphuric acid. It cannot be obtained free from water. Its solution, if confined with a vessel of sulphuric acid under the exhausted receiver of an air-pump, may be concentrated till it has a density of 1·347; but if an attempt is made to condense it still further, the acid is decomposed, sulphurous acid gas escapes, and sulphuric acid remains in solution. A similar change is still more readily produced if the evaporation is conducted by heat.

Welter and Gay-Lussac analyzed hyposulphuric acid by exposing neutral hyposulphate of baryta to heat. At a temperature a little above 212° this salt suffers complete decomposition; sulphurous acid gas is disengaged, and neutral sulphate of baryta is obtained. It was thus ascertained that 72 grains of hyposulphuric acid yield 32 grains of sulphurous, and 40 of sulphuric acid; from which it is inferred that hyposulphuric acid is composed either of an equivalent of each of those acids combined with each other, or of 2 eq. of sulphur and 5 of oxygen.

SECTION VIII.

PHOSPHORUS.

Hist. and Prep.—Phosphorus (*φωσφόρος*, from *φῶς light* and *φέρειν to carry*), so called from its property of shining in the dark, was discovered about the year 1669 by Brandt, an alchemist of Hamburgh. It was originally prepared from urine; but Scheele, after Gahn's discovery of bones containing phosphate of lime, extracted it from that source. The bones are first ignited in an open fire till they become white, so as to destroy their animal matter, and burn away the charcoal derived from it, in which state they contain nearly 4-5ths of phosphate of lime. They are then reduced to a fine powder, and digested for a day or two with half their weight of strong sulphuric acid, with the addition of so much water as will give the consistence of a thin paste. Decomposition of the phosphate of lime is thus effected, and two new salts formed, the sparingly soluble sulphate and a soluble superphosphate of lime. The latter is dissolved in warm water, and the solution, after being separated by filtration from the sulphate of lime, is evaporated to the consistence of syrup, mixed with a fourth of its weight of powdered charcoal, and strongly heated in an earthen retort well luted with clay. The beak of the retort is put into water, in which the phosphorus, as its vapour passes over, is condensed. When first obtained it is usually of a reddish brown colour, owing to the presence of phosphuret of carbon formed during the process. It may be purified by fusion in hot water, and being pressed while liquid through chamois leather, or by a second distillation.

In this process the oxygen of that part of the phosphoric acid which constitutes the superphosphate, unites with charcoal, giving rise to carbonic acid and carbonic oxide gases; and phosphate of lime in the state of bone earth, together with redundant charcoal, remains in the retort. The lime acts an important part in fixing the phosphoric acid, which if not so combined would distil over before the heat was high enough for its decomposition. In extracting phosphorus from urine, the phosphoric acid should be thrown down by acetate of the oxide of lead, and the insoluble salt converted by the action of sulphuric acid into the superphosphate, which is decomposed by charcoal as in the former process.

Prop.—When pure, transparent and almost colourless. At common temperatures it is a soft solid of sp. gr. 1·77; is easily cut with a knife, and the cut surface has a waxy lustre: at 108° it fuses, and at 550° is converted into vapour, which according to Dumas has a sp. gr. of 4·355. It is soluble by the aid of heat in naphtha, in fixed and volatile oils, in the chloride of sulphur, sulphuret of carbon, and sulphuret of phosphorus. On its cooling from solution in the latter, Mitscherlich obtained it in regular dodecahedral crystals. By the fusion and slow cooling of a large quantity of phosphorus, M. Frantween has obtained very fine crystals of an octohedral form, and as large as a cherry-stone. Thenard has remarked that when phosphorus is fused at 150°, and suddenly cooled by being plunged into cold water, it appears black; but by fusion and slow cooling it recovers its original aspect.

It is exceedingly inflammable. Exposed to the air at common temperatures, it undergoes slow combustion, emits a white vapour of a peculiar alliaceous odour, appears distinctly luminous in the dark, and is gradually consumed. On this account, phosphorus should always be kept under water. The disappearance of oxygen which accompanies these changes is shown by putting a stick of phosphorus in a jar full of air, inverted over water. The volume of the gas gradually diminishes; and if the temperature of the air is at 60°, the whole of the oxygen will be withdrawn in the course of 12 or 24 hours. The residue is nitrogen gas, containing about 1-40th of its bulk of the vapour of phosphorus. It is remarkable that the slow combustion of phosphorus does not take place in pure oxygen, unless its temperature be about 80°. But if the oxygen be diluted with nitrogen, hydrogen, or carbonic acid gases, the oxidation occurs at 60°; and it takes place at temperatures still lower in a vessel of pure oxygen, rarefied by diminished pressure. Mr. Graham finds that the presence of certain gaseous substances, even in minute quantity, has a remarkable effect in preventing the slow combustion of phosphorus: thus at 66° it is entirely prevented by the presence, (Quart. Jour. of Science, N. S. vi. 83,)

			Volumes of air.
of 1	volume	of olefiant gas in . .	450
1	ditto	of vapour of sulphuric ether in .	150
1	ditto	of vapour of naphtha in .	1820
1	ditto	of vapour of oil of turpentine in .	4444,

and by an equally slight impregnation of the vapour of the other essential oils. Their influence is not confined to low temperatures.

Phosphorus becomes faintly luminous in the dark, in mixtures of

1 volume of air	and 1 volume of olefiant gas at .	200° F.
1 . .	and 1 ditto of vapour of ether at .	215°
111 . .	and 1 ditto of vapour of naphtha at	170°
156 . .	and 1 ditto of vapour of turpentine at	186°.

It may be sublimed at its boiling temperature, in air containing a considerable proportion of the vapour of oil of turpentine, without diminishing the quantity of oxygen present, provided the heat be gradually and uniformly applied. Mr. Graham has also remarked, that the oxidation of phosphorus in the air is promoted by the presence of hydrochloric acid gas.

A very slight degree of heat is sufficient to inflame phosphorus in the open air. Gentle pressure between the fingers, friction, or a temperature not much above its point of fusion, kindles it readily. It burns rapidly even in the air, emitting a splendid white light, and causing intense heat. Its combustion is far more rapid in oxygen gas, and the light proportionally more vivid.

When phosphorus is kept for a long time under water, especially if exposed to light, its surface acquires a thin coating of white matter, which some have described as an oxide, and others as a hydrate of phosphorus. It seems according to Rose to be neither an oxide nor a hydrate, but phosphorus in a peculiar mechanical state, which deprives it of its usual action upon light, and renders it opaque. (Pog. Annalen, xxvii. 565.)

Repeated researches by Berzelius have shown that the oxygen in phosphorus and phosphoric acids is in the ratio of 3 to 5, a result conformable to experiments on the same subject by Dulong, and admitted by most chemists. It is hence inferred that the smallest molecule of phosphoric acid contains 5 atoms of oxygen. Also Berzelius finds that 31·4 parts of phosphorus require 40 of oxygen for forming phosphoric acid: if this acid consist of one atom of phosphorus and five atoms of oxygen, 31·4 will represent one atom of phosphorus; or if the acid contain 2 atoms to 5, the atom of phosphorus will be half 31·4 or 15·7. It is doubtful which view is preferable, and I therefore continue to use the latter.

Its equivalent is therefore 15·7; eq. vol. = 25; symb. P.

The compounds of phosphorus described in this section are the following:—

	Phosp.	Oxy.	Equiv.	Formulæ.
Oxide of Phosphorus	47·1 or 3 eq. +	8 or 1 eq.	= 55·1	$3P + O$ or P_3O
Hypophosphorus acid	31·4 or 2 eq. +	8 or 1 eq.	= 39·4	$2P + O$ or P_2O
Phosphorus acid	31·4 or 2 eq. +	24 or 3 eq.	= 55·4	$2P + 3O$ or P_2O_3
Phosphoric acid Pyrophosphoric acid Metaphosphoric acid	31·4 or 2 eq. +	40 or 5 eq.	= 71·4	$2P + 5O$ or P_2O_5

COMPOUNDS OF OXYGEN AND PHOSPHORUS.

Oxide.—When a jet of oxygen gas is thrown upon phosphorus while in fusion under hot water, combustion ensues, phosphoric acid is formed, and a number of red particles collect, which have been examined by M. Pelouze, who has shown them to be an oxide of phosphorus. The red matter left when phosphorus is burned, is probably of the same nature.

This, the only known oxide of phosphorus, is of a red colour, without taste or odour, and is insoluble in water, ether, alcohol, and oil. It is permanent in the air, even at 662° F., but takes fire at a low red heat. Heated to redness in a tube, phosphorus is expelled, and metaphosphoric acid remains. It takes fire in chlorine gas, and is rapidly oxidized by nitric acid. It does not appear to possess any alkaline character. (An. de Ch. et Ph. l. 83.) Its equivalent is 55·1; symb. $3P + O$, or P_3O.

Hypophosphorous Acid.—This acid was discovered in 1816 by Dulong. (An. de Ch. et Ph. ii.) When water acts upon the phosphuret of barium the elements of both enter into a new arrangement, giving rise to phosphuretted hydrogen, phosphoric acid, hypophosphorous acid, and baryta. The former escapes in the form of gas, and the two latter combine with the baryta. Hypophosphite of baryta, being soluble, dissolves in the water, and may consequently be separated by filtration from the phosphate of baryta, which is insoluble. On adding a sufficient quantity of sulphuric acid for precipitating the baryta, hypophosphorous acid is obtained in a free state, and on evaporating the solution, a viscid liquid remains, highly acid and even crystallizable, which is a *hydrate of hypophosphorous acid.* When exposed to heat in close vessels, it undergoes the same kind of change as hydrated phosphorous acid.

Prop.—It is a powerful deoxidizing agent. It unites with alkaline bases; and it is remarkable that all its salts are soluble in water. The hypophosphites of potassa, soda, and ammonia, dissolve in every proportion in rectified alcohol; and hypophosphite of potassa is even more deliquescent than chloride of calcium. They are all decomposed by heat, and yield the same products as the acid itself. They are conveniently prepared by precipitating hypophosphite of baryta, strontia, or lime, with the alkaline carbonates; or by directly neutralizing these carbonates with hypophosphorous acid. The hypophosphite of baryta, strontia, and lime, are formed by boiling these earths in the caustic state in water together with fragments of phosphorus. The same change occurs as during the action of water on phosphuret of barium. The composition of this acid, as stated at page 255, is on the authority of Rose. (Poggen. Annalen, ix. 367.) Its eq. is 39·4; symb. $2P + O$, $\underline{\dot{P}}$, or P_2O.

Phosphorous Acid.—Prep.—When phosphorus is burned in air highly rarefied, imperfect oxidation ensues, and metaphosphoric and phosphorous acids are generated, the latter being obtained in the form of a white volatile powder. It may be procured more conveniently by subliming phosphorus through powdered bichloride of mercury contained in a glass tube; when a limpid liquid comes over, which is a compound of chlorine and phosphorus. (Davy's Elements, p. 288.) This substance and water mutually decompose each other: the hydrogen of water unites with the chlorine, and forms hydrochloric acid; while the oxygen attaches itself to the phosphorus, and thus phosphorous acid is produced. The solution is then evaporated to the consistence of syrup to expel the hydrochloric acid; and the residue, which is hydrate of phosphorous acid, becomes a crystalline solid on cooling. It is also generated during the slow oxidation of phosphorus in atmospheric air. The product attracts moisture from the air, and forms an oil-like liquid. Dulong thinks that a distinct acid is produced in this case, which he calls *phosphatic acid;* but the opinion of Davy, that it is merely a mixture of phosphoric and phosphorous acids, is, in my opinion, perfectly correct.

Prop.—When obtained by the first process, it is anhydrous. Heated in the open air, it takes fire and forms metaphosphoric acid; but in close vessels it is resolved into metaphosphoric acid and phosphorus. The action of the hydrate under the latter circumstances is different, owing to the reaction of the elements of the water and acid, by which metaphosphoric acid and a gaseous compound of phosphorus and hydrogen are produced. The nature of this gas will be more particularly noticed in the section on phosphuretted hydrogen. It dissolves readily in water, has a sour taste, and smells somewhat like garlic. It unites with alkalies, and forms salts which are termed *phosphites.* The solution of phosphorous acid absorbs oxygen slowly from air, and is converted into phosphoric acid. From its tendency to unite with an additional quantity of oxygen, it is a powerful deoxidizing agent; and hence, like sulphurous acid, precipitates mercury, silver, platinum, and gold, from their saline combinations in the metallic form. Nitric acid converts it into phosphoric acid.

Its eq. is 55·4; symb. $2P + 3O$, $\underline{\dddot{P}}$, or P_2O_3.

Phosphoric Acid.—Hist.—It was shown in the year 1827 by Dr. Clark, now Professor of Chemistry in Aberdeen, that under the term *phosphoric acid* had previously been confounded two distinct acids, one of which he proposed to distinguish by the name *pyrophosphoric acid* (from πυρ *fire*), to indicate that it is phosphoric acid modified by heat; and very lately Mr. Graham has described another modification of phosphoric acid, to which he has given the provisional name of metaphosphoric (from μετα *together with*), implying phosphoric acid and something besides; but this name is rather unfortunate, since it is applied to the only one of the three modifications which can be obtained free from water. Perhaps paraphosphoric (from παρα *near to*) would be more appropriate. These three acids contain phosphorus and oxygen in the same ratio, and have the same equivalent, so that they may be considered as isomeric bodies (page 183); but that difference in the arrangement of their elements on which their peculiarities may be presumed to depend is very slight, since they are easily convertible into each other. Mr. Graham, indeed, supposes the difference to arise solely from a disposition to unite in different proportions with water and alkaline bases; but this view scarcely suffices as an explanation, because it does not account for the peculiar *disposition* which causes their distinctive characters. (Phil. Trans. 1833, Part ii., and Phil. Mag. 3rd Series, iv. 401.)

Prep.—Phosphoric acid has hitherto been obtained only in combination with water or some alkaline base. One of the best modes for procuring it, is to oxidize phosphorus by strong nitric acid; but in this process care is necessary, as the action is sometimes very violent, and the escape of binoxide of nitrogen gas ungovernably rapid. It is safely conducted by adding fragments of phosphorus, or the so-called phosphatic acid, to strong nitric acid contained in a platinum crucible partially closed by its cover. Gentle heat is applied so as to commence, and, when necessary, to maintain moderate effervescence; and when one portion of phosphorus disappears, another is added, till the whole of the nitric acid is exhausted. The solution is then evaporated to dryness, and exposed to a red heat to expel the last traces of nitric acid. This should always be done in vessels of platinum, since phosphoric acid acts chemically upon those of glass or porcelain, and is thereby rendered impure. In this case, as in some other instances of the oxidation of combustibles by nitric acid, water is decomposed; and while its oxygen unites with phosphorus, its hydrogen combines with nitrogen of the nitric acid. A portion of ammonia, thus generated, is expelled by heat in the last part of the process.

Phosphoric acid may be prepared at a much cheaper rate from bones. For this purpose, superphosphate of lime, obtained in the way already described, should be boiled for a few minutes with excess of carbonate of ammonia. The lime is thus precipitated as a phosphate, and the solution contains phosphate, together with a little sulphate, of ammonia. The liquid, after filtration, is evaporated to dryness, and then ignited in a platinum crucible, by which means the ammonia and sulphuric acid are expelled.

In both the foregoing processes phosphoric acid exists only in solution; for on heating to redness, in order to expel ammonia in the one case, and nitric acid in the other, metaphosphoric acid is generated. To reproduce the phosphoric acid, the residue in the crucible requires to be dissolved in water and boiled for a few minutes.

Prop.—Phosphoric acid is colourless, intensely sour to the taste, reddens litmus strongly, and neutralizes alkalies; but it does not destroy the texture of the skin, like sulphuric and nitric acids. Its solution may be evaporated at a temperature of 300° without decomposition, and when thus concentrated it assumes a dark colour, is as thick as treacle when cold, and consists of 71·4 parts or 1 eq. of phosphoric acid and 27 parts or 3 eq. of water. Mr. Graham obtained this hydrate in thin crystalline plates, which were extremely deliquescent, by keeping it for seven days *in vacuo* along with sulphuric acid. On heating this hydrate for several days to 415°, it lost nearly two-thirds of an equivalent of water, and then principally consisted of pyrophosphoric acid with two equivalents of water. At a still higher temperature metaphosphoric acid began to be formed; and at a red heat the conversion was complete. But after ignition it still contains water, amounting, according to Rose, to 9·44 per cent., which is rather more than an equivalent of water to one of metaphosphoric acid.

Phosphoric acid is remarkable for its tendency to unite with alkaline bases, in such proportions that the oxygen of the base and of the acid is as 3 to 5; or, in other words, it is prone to form subsalts, in which one equivalent of acid is combined with three equivalents of base. It manifests the same character in regard to water, and ceases to be phosphoric acid unless three equivalents of water to one of acid are present: it even appears that the water acts the part of a base, hence called *basic* water, and that the aqueous solution is not a mere solution of phosphoric acid, but of triphosphate of water, a sort of salt composed of one equivalent of acid and three equivalents of water. Part of this basic water enters along with soda into the constitution of two of the phosphates of soda, the water and soda together forming the three equivalents of base required by one equivalent of the acid. This point will be more fully described in the history of the phosphates.

When phosphoric acid is neutralized by ammonia and mixed with nitrate of oxide of silver, the yellow phosphate of that oxide subsides; a character by which it is distinguished from pyrophosphoric and metaphosphoric acids, as well as from all other acids except the arsenious. A certain test between phosphoric and arsenious acids is, that the former is neither changed in colour nor precipitated when a stream of hydrosulphate acid gas is transmitted through it; while the latter, with the required precautions, first acquires a yellow tint, and then yields a yellow precipitate.

Its eq. is 71·4; symb. $2P + 5O$, $\underline{\overset{\cdot\cdot\cdot\cdot\cdot}{P}}$, or P_2O_5: but as it cannot exist uncombined, it is best denoted by $X_3 . P_2O_5$, where X represents an equivalent of water or any base.

Pyrophosphoric Acid.—This acid is formed by exposing concentrated phosphoric acid for some time to a heat of 415°. Its general characters resemble phosphoric acid; but when neutralized by ammonia and mixed with nitrate of oxide of silver it yields a snow-white granular precipitate, pyrophosphate of that oxide, by which it is distinguished from phosphoric and metaphosphoric acids. In solution with cold water pyrophosphoric acid passes gradually, and at a boiling temperature rapidly, into phosphoric acid. Its salts, while neutral, are very permanent; but when boiled with either of the stronger acids in water, they are quickly converted more or less completely into phosphates.

Pyrophosphoric acid is remarkable for its tendency to unite with two equivalents of a base. Its aqueous solution probably contains a dipyrophosphate of water, that is, 1 eq. of the acid with 2 eq. of water, expressed by $2HO + P_2O_5$, or $2HO . P_2O_5$. This basic water is readily displaced by 2 eq. of stronger bases, such as soda;

or if 1 eq. only of soda be added, then the soda and water together make up the 2 eq. of base, the formula of the salt being NaO, HO. P_2O_5. The readiest mode of obtaining a pyrophosphate is to heat phosphoric acid with any fixed base in the ratio of one to two of their equivalents. This was done by Dr. Clark in the experiments by which he established the existence of pyrophosphoric acid. (Brewster's Journal, vii. 298.) Phosphate of soda is a compound of 1 eq. phosphoric acid, 2 eq. soda, 1 eq. basic water, and 24 eq. water of crystallization, its formula being $2NaO$, HO. $P_2O_5 + 24HO$: on drying this salt its water of crystallization is expelled, there remains $2NaO$, HO. P_2O_5, which is still a phosphate, but on heating to redness the basic water is expelled, and $2Na$. P_2O_5, pyrophosphate of soda, remains. By being forced to unite with 2 eq. of base, the acid acquires a disposition to do so on all occasions.

Its eq. is 71·4: symb. X_2. P_2O_5, X being used as above.

Metaphosphoric Acid.—This acid is obtained by burning phosphorus in dry air or oxygen gas, or heating to redness a concentrated solution of phosphoric or pyrophosphoric acids. By the former method the acid is a white solid, and anhydrous; in the latter it is a hydrate, or probably a metaphosphate of water, composed of 1 eq. acid and 1 eq. of water, its formula being HO. P_2O_5. The water in this compound cannot be expelled by fire, since on attempting to do so by a violent heat, the whole is sublimed. In an open crucible it volatilizes at a temperature by no means high.

The peculiarity of this acid is to combine with one equivalent of a base. On exposing the anhydrous acid to the air it rapidly deliquesces, and at the same time acquires its basic water, which can only be replaced by an equivalent quantity of soda or some other alkaline base. The water is also driven off by fusion with siliceous or aluminous substances with which the acid unites and forms very fusible compounds. The pure hydrated acid is of itself very fusible, and on cooling concretes into a transparent brittle solid, being known under the name of *glacial phosphoric acid*, which is highly deliquescent, and can hence only be preserved in its glassy state in bottles carefully closed.

The metaphosphoric resembles pyrophosphoric acid in the facility with which its aqueous solution passes into phosphoric acid. On the contrary, both of the other acids are converted into metaphosphates when heated to redness in contact with no more than one equivalent of certain fixed bases, such as potassa and soda. This acid when free occasions precipitates in solutions of the salts of baryta, and most of the earths and metallic oxides, and forms an insoluble compound with albumen. The metaphosphate of baryta and oxide of silver both fall in gelatinous flakes of a grey colour. Its eq. is 71·4; symb. P_2O_5, or X. P_2O_5.

In an admirable paper on the constitution of the organic acids, Liebig has shown, that, if we adopt the view first suggested by Davy, and afterwards by Dulong, namely, that the hydrated acids, as well as the hydracids, are all compounds of hydrogen, we can easily understand how the three forms of phosphoric acid differ from each other. On this view, just as hydrochloric acid is H,Cl, hydrated sulphuric acid is H,SO_4. In like manner metaphosphoric acid is H,P_2O_6; pyrophosphoric acid is H_2,P_2O_7, and common phosphoric acid is H_3,P_2O_8. They are thus distinct compounds, as is evident from the differences among their salts. When the hydrogen in them is replaced, equivalent for equivalent, by a metal, a salt is formed; and we thus see how the salts of metaphosphoric acid contain 1 eq. of metal, those of pyrophosphoric acid 2 eq., and those of common phosphoric acid 3 eq. of metal. The first is a monobasic acid, the second a bibasic, and the third a tribasic acid. The memoir of Liebig just referred to (Ann. der Pharm. vol. xxvi.) has placed beyond question the existence of polybasic acids; that is, acids which combine with more than one equivalent of base to form neutral salts. This subject will be more fully discussed hereafter.

SECTION IX.

BORON.

Hist. and Prep.—Sir H. Davy discovered the existence of *Boron* in 1807 by exposing boracic acid to the action of a powerful galvanic battery; but he did not obtain a sufficient supply of it for determining its properties. Gay-Lussac and Thenard * procured it in greater quantity in 1808 by heating boracic acid with potassium. The boracic acid is by this means deprived of its oxygen, and boron is set free. The easiest and most economical method of preparing this substance, according to Berzelius, is to decompose borofluoride of potassium or sodium by means of potassium. (Annals of Philosophy, xxvi. 128.)

---

* Recherches Physico-Chimiques, vol. i.

Prop.—It is a dark olive-coloured substance, which has neither taste nor smell, and is a non-conductor of electricity. It is insoluble in water, alcohol, ether, and oils. It does not decompose water whether hot or cold. It bears intense heat in close vessels, without fusing or undergoing any other change except a slight increase of density. Its sp. gr. is about twice as great as that of water. It may be exposed to the atmosphere at common temperatures without change; but if heated to 600°, it suddenly takes fire, oxygen gas disappears, and boracic acid is generated. It is very difficult to oxidize all the boron by burning, because the boracic acid fuses at the moment of being formed, and by glazing the surface of the unburned boron protects it from oxidation. It also passes into boracic acid when heated with nitric acid, or with any substance that yields oxygen with facility.

According to the experiments of Davy and Berzelius, boron in burning unites with 68 per cent. of oxygen; and the latter, from the composition of borax, estimates the oxygen in boracic acid at 68·8 per cent. In this, as in some other cases, where a combustible unites with oxygen in one proportion only, it is difficult with any certainty to assign the true atomic constitution of the compound. Boracic acid may be a compound of boron and oxygen in the ratio of 1 atom to 1 atom, in that of 1 to 2 as supposed by Thomson, or of 1 to 3. When dry boracic acid is heated with charcoal in chlorine gas, it is decomposed, and two volumes of chloride of boron and three of carbonic oxide gas are produced. The latter contains 1½ volumes of oxygen, and the former has been proved by Dumas to be composed of 3 volumes of chlorine united with 1 volume of the vapour of boron, the density of which is estimated at ·751, its eq. vol. being 100. From this it may be deduced that the constitution of boracic acid is BO_3, which has also been recently adopted by Berzelius (Pog. An. xxiv. 561). Hence its eq. is 10·9; eq. vol. = 100; symb. B.

Boracic Acid.—Hist. and Prep.—This is the only known compound of boron and oxygen. As a natural product it is found in the hot springs of Lipari, and in those of Sasso in the Florentine territory. It is a constituent of several minerals, among which the datolite and boracite may in particular be mentioned. It occurs much more abundantly under the form of borax, a native compound of boracic acid and soda. It is prepared for chemical purposes by adding sulphuric acid to a solution of purified borax in about four times its weight of boiling water, till the liquid acquires a distinct acid reaction. The sulphuric acid unites with the soda; and the boracic acid is deposited, when the solution cools, in a confused group of shining scaly crystals. It is then thrown on a filter, washed with cold water to separate the adhering sulphate of soda and sulphuric acid, and still further purified by solution in boiling water and re-crystallization. But even after this treatment it is apt to retain a little sulphuric acid; on this account, when required to be absolutely pure, it should be fused in a platinum crucible, and once more dissolved in hot water and crystallized.

Prop.—In the crystallized state it is a hydrate, which contains 43·62 per cent. of water, being a ratio of 34·9 parts or 1 eq. of the anhydrous acid to 27 parts or 3 eq. of water. This hydrate dissolves in 25·7 times its weight of water at 60°, and in 3 times at 212°. Boiling alcohol dissolves it freely, and the solution, when set on fire, burns with a beautiful green flame; a test which affords the surest indication of the presence of boracic acid. Its sp. gr. is 1·479. It has no odour, and its taste is rather bitter than acid. It reddens litmus paper feebly, and effervesces with alkaline carbonates. Faraday has noticed that it renders turmeric paper brown like the alkalies. From the weakness of the acid properties of boracic acid, all the borates, when in solution, are decomposed by the stronger acids; and the neutral borates of potash and soda are deprived of half their base by carbonic acid, at common temperatures.

When hydrous boracic acid is exposed to a gradually increasing heat in a platinum crucible, its water of crystallization is wholly expelled, and a fused mass remains which bears a white heat without being sublimed. On cooling, it forms a hard, colourless, transparent glass, which is anhydrous boracic acid. If the water of crystallization be driven off by the sudden application of a strong heat, a large quantity of boracic acid is carried away during the rapid escape of watery vapour. The same happens, though in a less degree, when a solution of boracic acid in water is boiled briskly. Vitrified boracic acid should be preserved in well-stopped vessels; for if exposed to the air it absorbs water, and gradually loses its transparency. Its sp. gravity is 1·803. It is exceedingly fusible, and communicates this property to the substances with which it unites. For this reason borax is often used as a flux.

Its eq. is 34·9; symb. $B + 3O$, $\dddot{B}$, or BO_3.

SECTION X.

SILICON.

Hist.—THAT silicic acid or silica is composed of a combustible body united with oxygen, was demonstrated by Davy; for on bringing the vapour of potassium in contact with pure silicic acid heated to whiteness, a silicate of potassa resulted, through which was diffused the inflammable base of silicic acid in the form of black particles like plumbago. To this substance, on the supposition of its being a metal, the term *silicium* was applied. But though this view has been adopted by most chemists, so little was known with certainty concerning the real nature of the base of silica, that Thomson inclined to the opinion of its being a non-metallic body, and accordingly associated it in his system of chemistry with carbon and boron under the name of *silicon.* The recent researches of Berzelius appear almost decisive of this question. A substance which has not the metallic lustre, and is a non-conductor of electricity, cannot be regarded as a metal.

Prep.—Pure silicon was first procured by Berzelius in the year 1824 by the action of potassium on fluosilicic acid gas, but it is more conveniently prepared from the double fluoride of silicon and potassium or sodium, previously dried by a temperature near that of redness. When this compound is heated in a glass tube with potassium, the latter unites with fluorine, and silicon is separated. The heat of a spirit-lamp is sufficient for the purpose, and the decomposition takes place, accompanied with feeble detonation, before the mixture becomes red-hot. When the mass is cold, the soluble parts are removed by the action of water; the first portions of which produce disengagement of hydrogen gas, owing to the presence of some silicuret of potassium. The silicon thus procured is chemically united with a little hydrogen, and at a red heat burns vividly in oxygen gas. In order to render it quite pure, it should be first heated to redness, and then digested in dilute hydrofluoric acid to dissolve adherent particles of silicic acid. (An. of Phil. xxvi. 116.)

Prop.—Silicon, obtained in this manner, has a dark nut-brown colour, without the least trace of metallic lustre. It is a non-conductor of electricity. It is incombustible in air and in oxygen gas; and may be exposed to the flame of the blowpipe without fusing or undergoing any other change. It is neither dissolved nor oxidized by the sulphuric, nitric, hydrochloric, or hydrofluoric acids;

but a mixture of the nitric and hydrofluoric acids dissolves it readily even in the cold.

It is not changed by ignition with chlorate of potassa. In nitre it does not deflagrate until the temperature is raised so high that the acid is decomposed; and then the oxidation is effected by the affinity of the disengaged alkali for silicic acid co-operating with the attraction of oxygen for silicon. For a similar reason it burns vividly when brought into contact with carbonate of potassa or soda, and the combustion ensues at a temperature considerably below that of redness. It explodes in consequence of a copious evolution of hydrogen gas, when it is dropped upon the fused hydrate of potassa, soda, or baryta.

Berzelius ascertained, by oxidizing a known weight of silicon, that 100 parts of silicic acid are composed of 48·4 of silicon and 51·6 of oxygen. Now, if silicic acid, as Thomson supposes, be composed of single atoms of its elements, then the equivalent of silicon will be 7·5; but if, as Berzelius believes, the smallest molecule of that acid contain 3 atoms of oxygen united with 1 atom of silicium, the equivalent of silicium would be 22·5. The latter view is supported by very strong analogies. Its equivalent is therefore 22·5; symb. Si.

Silicic Acid.—Hist. and Prep.—This compound, known also by the names of *silica* and *siliceous earth*, exists abundantly in nature. It enters into the composition of most of the earthy minerals; and under the name of quartz rock, forms independent mountainous masses. It is the chief ingredient of sandstones, flint, calcedony, rock crystal, and other analogous substances. It may indeed be procured, of sufficient purity for most purposes, by igniting transparent specimens of rock crystal, throwing them while red-hot into water, and then reducing them to powder.

Prop.—Pure silicic acid, in this state, is a light white powder, which feels rough and dry when rubbed between the fingers; is both insipid and inodorous; the sp. gr. is 2·69. It is fixed in the fire, and very infusible; but fuses before the oxy-hydrogen blowpipe with greater facility than lime or magnesia. It is quite insoluble in water; but Berzelius has shown, that if presented to water while in the nascent state, it is dissolved in large quantity. On evaporating the solution gently, a bulky gelatinous hydrate separates, which is partially decomposed by a very moderate temperature, but does not part with all its water except at a red heat.

Silicic acid has no action on test paper; but in all its chemical relations it manifests the properties of an acid, and displaces carbonic acid by the aid of heat from the alkalies. Its combinations with the fixed alkalies are effected by mixing pure sand with carbonate of potassa or soda, and heating the mixture to redness. During the process, carbonic acid is expelled, and a silicate of the alkali is generated. The nature of the product depends upon the proportions which are employed. On igniting one part of silicic acid with three of carbonate of potassa, a vitreous mass is formed, which is deliquescent, and may be dissolved completely in water. This solution, which was formerly called *liquor silicum*, has an alkaline reaction, and absorbs carbonic acid on exposure to the atmosphere, by which it is partially decomposed. Concentrated acids precipitate the silicic acid as a gelatinous hydrate; but if a considerable quantity of water is present, and the acid is added gradually, the alkali may be perfectly neutralized without any separation of silicic acid. When a solution of this kind is evaporated to dryness, the silicic acid is rendered quite insoluble, and may thus be obtained in a pure form.

But if the proportion of silicic acid and alkali be reversed, a transparent brittle compound results, which is insoluble in water, is attacked by none of the acids excepting the hydrofluoric, and possesses the well-known properties of glass. Every kind of ordinary glass is a silicate, and all its varieties are owing to differences in the proportion of the constituents, to the nature of the alkali, or to the presence of foreign matters. Thus, green bottle glass is made of impure materials, such as river sand, which contains iron, and the most common kind of kelp or pearl-ashes. Crown glass for windows is made of a purer alkali, and sand which is free from iron. Plate glass, for looking-glasses, is composed of sand and alkali in their purest state; and in the formation of flint-glass, besides these pure ingredients, a considerable quantity of litharge or red lead is employed. A small portion of peroxide of manganese is also used, in order to oxidize carbonaceous matters contained in the materials of the glass; and nitre is sometimes added with the same intention. Ordinary flint-glass, according to Faraday, contains 51·93 per cent. of silicic acid, 33·28 of oxide of lead, and 13·77 of potassa; proportions which correspond to 1 eq. of potassa, 1 eq. of oxide of lead, and nearly 4 eq. of silicic acid. Flint-glass, accordingly, is a double salt, consisting chiefly of bisilicate of potassa and bisilicate of oxide of lead.

Its eq. is 46·5; symb. $Si + 3O$, $\dddot{Si}$, or SO_3.

SECTION XI.

SELENIUM.

Hist. and Prep.—This substance was discovered in 1818 by Berzelius, who called it selenium, from Σελήνη *the Moon*, suggested by its having at first been mistaken for the metal tellurium. (An. de Ch. et Ph. ix. 160, and An. of Phil. xiii. 401.) It has hitherto been obtained in very small quantity, and occurs for the most part in combination with some varieties of iron pyrites. Stromeyer has also detected it, as a sulphuret of selenium, among the volcanic products of the Lipari isles. It is found likewise at Clausthal in the Hartz, combined, according to Stromeyer and Rose, with several metals, such as lead, cobalt, silver, mercury, and copper. Berzelius found it in the sulphur obtained by sublimation from the iron pyrites of Fahlun. In a manufactory of sulphuric acid, at which this sulphur was employed, it was observed that a reddish-coloured matter always collected at the bottom of the leaden chamber; and on burning this substance, Berzelius perceived a strong and peculiar odour, similar to that of decayed horse-radish, which induced him to submit it to a careful examination, and thus led to the discovery of selenium. For the extraction of selenium from the native sulphuret, Magnus proposes to mix it with eight times its weight of peroxide of manganese, and to expose the mixture to a low red heat in a glass retort, the beak of which dips into water. The sulphur, oxidized at the expense of the manganese, escapes in the form of sulphurous acid; while the selenium either sublimes as such or in the state of selenious acid. Should any of the latter be carried over into the water, it would there be reduced by the sulphurous acid.

Prop.—Selenium, at common temperatures, is a brittle opaque solid body, without taste or odour. It has a metallic lustre and the aspect of lead, when in mass; but it is of a deep red colour when reduced to powder. Its sp. gr. is between 4·3 and 4·32. At 212° it softens, and is then so tenacious, that it may be drawn out into fine threads which are transparent, and appear red by transmitted light. It becomes quite fluid at a temperature somewhat above that of boiling water. It boils at about 650°, forming a vapour which has a deep yellow colour, but is free from odour. It may be sublimed in close vessels without change, and condenses again into dark globules of a metallic lustre, or as a cinnabar-red powder, according as the space in which it collects is small or large. Berzelius at first regarded it as a metal; but, since it is an imperfect conductor of heat and electricity, it more properly belongs to the class of the simple non-metallic bodies.

Selenium is insoluble in water. It suffers no change from mere exposure to the atmosphere; but if heated in the open air, it combines readily with oxygen, and two compounds, oxide of selenium and selenious acid, are generated. If exposed to the oxidizing part of the blowpipe flame, it tinges the flame with a light blue colour, and exhales so strong an odour of decayed horse-radish, that 1-50th of a grain is said to be sufficient to scent the air of a large apartment. By this character the presence of selenium, whether alone or in combination, may always be detected.

Berzelius has shown that selenic acid is composed of 24 parts of oxygen and 39·6 of selenium. This substance, also, has three grades of oxidation, the oxygen in the two last of which is in the ratio of 2 and 3; and the highest grade, selenic acid, has in all its chemical relations a singularly close analogy to sulphuric acid. From these facts it is inferred that selenic acid is composed of 1 atom of selenium and 3 atoms of oxygen. Its eq. is 39·6; symb. Se.

The compounds of selenium described in this section are the following:—

	Selenium.	Oxygen.	Equiv.	Formulæ.
Oxide of Selenium (probably)	39·6 or 1 eq.	+ 8 or 1 eq.	= 47·6	SeO.
Selenious Acid	39·6	+ 16 or 2 eq.	= 55·6	SeO_2.
Selenic Acid	39·6	+ 24 or 3 eq.	= 63·6	SeO_3.

Oxide of Selenium.—This compound is formed in greatest abundance by heating selenium in a limited quantity of atmospheric air, and by washing the product to separate selenious acid, which is generated at the same time. It is a colourless gas, which is very sparingly soluble in water, and does not possess any acid properties. It is the cause of the peculiar odour which is emitted during the oxidation of selenium.

Selenious Acid.—This acid is most conveniently prepared by digesting selenium in nitric or nitro-hydrochloric acid till it is completely dissolved. On evaporating the solution to dryness, a white residue is left, which is selenious acid. By increase of temperature, the acid itself sublimes, and condenses again unchanged into long four-sided needles. It attracts moisture from the air, whereby it suffers imperfect liquefaction. It dissolves in alcohol and water. It has distinct acid properties, and its salts are called *selenites.*

Selenious acid is readily decomposed by all substances which have a strong affinity for oxygen, such as sulphurous and phosphorous acids. When sulphurous acid, or an alkaline sulphite, is added to a solution of selenious acid, a red-coloured powder, pure selenium, is thrown down, and the sulphurous is converted into sulphuric acid. Hydrosulphuric acid also decomposes it; and an orange-yellow precipitate subsides, which is a sulphuret of selenium.

Selenic Acid.—Hist.—The preceding compound, discovered by Berzelius, was till lately the only known acid of selenium, and has been described in elementary works under the name of selenic acid; but the recent discovery of another acid of selenium containing more oxygen than the other, has rendered necessary a change of nomenclature. The existence of selenic acid was first noticed by M. Nitzsch, assistant of Mitscherlich, and its properties have been examined and described by the Professor himself. (Edin. Journal of Science, viii. 294.)

Prep.—This acid is prepared by fusing nitrate of potassa or soda with selenium, a metallic seleniuret, or with selenious acid or any of its salts. Seleniuret of lead, as the most common ore of selenium, will generally be employed; but it is very difficult to obtain pure selenic acid by its means, because it is commonly associated with metallic sulphurets. The ore is first treated with hydrochloric acid to remove any carbonate that may be present; and the insoluble part, which is about a third of the mass, is mixed with its own weight of nitrate of soda, and thrown by successive portions into a red-hot crucible. The lead is thus oxidized, and the selenium converted into selenic acid, which unites with soda. The fused mass is then acted on by hot water, which dissolves only seleniate of soda, together with nitrate and nitrite of soda; while the insoluble matter, when well washed, is quite free from selenium. The solution is next made to boil briskly, when anhydrous seleniate of soda is deposited; while, on cooling, nitrate of soda crystallizes. On renewing the ebullition and subsequent cooling, fresh portions of seleniate and nitrate are procured; and these successive operations are repeated, until the former salt is entirely separated. This process is founded on the fact, that seleniate of soda, like the sulphate of the same base, is more soluble in water of about 90° than at higher or lower temperatures. The nitrite of soda, formed during the fusion, is purposely reconverted into nitrate by digestion with nitric acid.

The seleniate of soda thus procured always contains a little sulphuric acid, derived from the metallic sulphurets of the ore; and it is not possible to separate this acid by crystallization. All attempts to separate it by means of baryta were likewise fruitless; and the only method of effecting this object is by reducing the selenic acid into selenium. This is done by heating a mixture of seleniate of soda with hydrochlorate of ammonia, when the sodium unites with chlorine, all the hydrogen with oxygen, and selenium and nitrogen are set free. This change will be more readily followed when stated in symbols;—thus

$$NaO, SeO_3, NH_3 \text{ and } HCl, \text{ yield } N, Se, 4HO \text{ and } NaCl.$$

The selenium which sublimes is quite free from sulphur. It is then converted by nitric acid into selenious acid, which should be neutralized with soda, and fused with nitre or nitrate of soda. The pure seleniate of soda, separated from the nitrate according to the foregoing process, is subsequently dissolved in water, and obtained in crystals by spontaneous evaporation.

To procure the acid in a free state, seleniate of soda is decomposed by nitrate of oxide of lead. The seleniate of that oxide, which is as insoluble as the sulphate, after being well washed, is exposed to a current of hydrosulphuric acid gas, which precipitates all the lead as a sulphuret, but does not decompose the selenic acid. The excess of the gas is driven off by heat, and pure selenic acid remains diluted with water. The absence of fixed substances may be proved by its being volatilized by heat without residue; and if free from sulphuric acid, it gives no precipitate with chloride of barium after being boiled with hydrochloric acid. Any nitric acid which may be present is expelled by concentrating the solution by means of heat.

Prop.—It is a colourless liquid, which may be heated to 536° without appreciable decomposition; but above that point decomposition commences, and it becomes rapid at 554°, giving rise to disengagement of oxygen and selenious acid. When concentrated by a temperature of 329°, its sp. gr. is 2·524; at 512° it is 2·60, and at 545° it is 2·625, but a little selenious acid is then present. When procured by the process above described, selenic acid always contains water, but it is very difficult to ascertain its precise proportion. Some acid, which had been heated higher than 536°, contained, subtracting the quantity of selenious acid present, 15·75 per cent. of water, which approximates to the ratio of one equivalent of water and one of the acid. It is certain that selenic acid is decomposed by heat before parting with all the water which it contains.

Selenic acid has a powerful affinity for water, and emits as much heat in uniting with it as sulphuric acid does. Like this acid it is not decomposed by hydrosulphuric acid, and hence this gas may be employed for decomposing seleniate of the oxides of lead or copper. With hydrochloric acid the change is peculiar; for on boiling the mixture mutual decomposition ensues, water and selenious acid are formed, and chlorine is set free; so that the solution, like *aqua regia*, is capable of dissolving gold and platinum. Selenic acid dissolves zinc and iron with disengagement of hydrogen gas, and copper with formation of selenious acid. It dissolves gold also, but not platinum. Sulphurous acid has no action on selenic acid, whereas selenious acid is easily reduced by it. Consequently, when it is wished to precipitate selenium from selenic acid, it must be boiled with hydrochloric acid before sulphurous acid is added.

Mitscherlich has observed, that selenic and sulphuric acids are not only analogous in composition and in many of their properties, but that the similarity runs through their compounds with alkaline substances, their salts resembling each other in chemical properties, constitution, and form.

SECTION XII.

CHLORINE.

Hist.—THE discovery of chlorine was made in the year 1774 by Scheele, while investigating the nature of manganese, and he described it under the name of *dephlogisticated marine acid*. The French chemists called it *oxygenized muriatic acid*, a term which was afterwards contracted to *oxy-muriatic acid*, from an opinion proposed by Berthollet that it is a compound of *muriatic acid* and *oxygen*. In 1809 Gay-Lussac and Thenard published an abstract of some experiments upon this substance, which subsequently appeared at length in their Recherches Physico-Chimiques, wherein they stated that oxy-muriatic acid might be regarded as a simple body, though they gave the preference to the doctrine advanced by

Berthollet. Davy engaged in the inquiry about the same time; and after having exposed oxy-muriatic acid to the most powerful decomposing agents which chemists possess, without being able to effect its decomposition, he communicated to the Royal Society an essay, in which he denied its compound nature; and he maintained that, according to the true logic of chemistry, it is entitled to rank with simple bodies. This view, which is commonly termed the *new theory of chlorine*, though strongly objected to at the time it was first proposed, is now universally received by chemists. The grounds of preference will hereafter be briefly stated.

Prep.—Chlorine gas is obtained by the action of hydrochloric acid on peroxide of manganese. The most convenient method of preparing it is by mixing concentrated hydrochloric acid, contained in a glass flask, with half its weight of finely powdered peroxide of manganese. Effervescence, owing to the escape of chlorine, takes place even in the cold; but the gas is evolved much more freely by the application of a moderate heat. It should be collected by displacement of air in dry bottles. The tube conducting the gas reaches to the bottom of the bottle, where the chlorine, being heavier than air, accumulates, and displaces it. When the bottle is full, which is known by the colour of the gas appearing at the mouth of the bottle, it is stopped with a greased stopper, and another bottle put in its place. As some hydrochloric acid gas commonly passes over with it, the chlorine should not be considered quite pure, till after being transmitted through water.

The theory of this process will be readily understood by first viewing the elements which act on each other, namely,—

Manganese .	27·7 or 1 eq.		Mn
Oxygen .	16	2 eq.	2 O
Perox. of Mang.	43·7 or 1 eq.		Mn+2O

Chlorine .	70·84 or 2 eq.	2Cl
Hydrogen .	or 2 eq.	2H
Hydrochl. acid	72·84 or 2 eq.	2(H+Cl);

and then inspecting the products derived from them, namely,

Manganese . .	27·7	Hydrogen	2	Chlorine 35·42 or 1 eq.
Chlorine . .	35·42	Oxygen	16	
Chlorine of Mang.	63·12	Water	18.	

In symbols,

MnO_2 and 2HCl yield MnCl, 2HO, and Cl.

The affinities which determine these changes are the mutual attraction of oxygen and hydrogen, and of chlorine and manganese.

When it is an object to prepare chlorine at the cheapest rate, as for the purposes of manufacture, the preceding process is modified in the following manner. Three parts of sea-salt are intimately mixed with one of peroxide of manganese, and to this mixture two parts of sulphuric acid, diluted with an equal weight of water, are added. By the action of sulphuric acid on sea-salt, hydrochloric acid is disengaged, which reacts, as in the former case, upon the peroxide of manganese; so that, instead of adding hydrochloric acid directly to the manganese, the materials for forming it are employed. In this process, however, the sulphates of soda and protoxide of manganese are generated, instead of chloride of manganese. Thus the materials which act on each other are MnO_2, NaCl, and $2SO_3$; and the products MnO. SO_3, NaO. SO_3, and Cl.

Prop.—Chlorine (from *χλωϱος green*) is a yellowish-green coloured gas, which has an astringent taste, and a disagreeable odour. It is one of the most suffocating of the gases, exciting spasm and great irritation of the glottis, even when considerably diluted with air. When strongly and suddenly compressed, it emits both heat and light, the latter being solely due, as in the case of air and oxygen, to the chlorine acting chemically on the oil with which the compressing apparatus is lubricated (An. de Ch. et Ph. xliv. 181). According to Davy, 100 cubic inches of dry chlorine at 30 B. and 60° F. weigh between 76 and 77 grains. Gay-Lussac and Thenard found the density of pure and dry chlorine to be 2·47, which gives 76·599 grains as the weight of 100 cubic inches at 60° F. and 30 B. Under the pressure of about four atmospheres it is a limpid liquid of a bright yellow colour, which does not freeze at the temperature of zero, and which assumes the gaseous form with the appearance of ebullition when the pressure is removed. Kemp finds that this liquid is a non-conductor of electricity.

Cold recently boiled water, at the common pressure, absorbs twice its volume of chlorine, and yields it again when heated. The solution, which is made by transmitting a current of chlorine gas through cold water, has the colour, taste, and most of the other properties of the gas itself. When moist chlorine gas is exposed to a cold of 32°, yellow crystals are formed, which consist of water and chlorine in definite proportions. They are composed, according to Faraday, of 35·42 parts or 1 eq. of chlorine, and 90 parts or 10 eq. of water. It experiences no chemical change from the action of the imponderables. Thus it is not affected chemically by intense heat, by strong shocks of electricity, or by a powerful galvanic battery. Davy exposed it also to the action of charcoal heated to whiteness by galvanic electricity, without separating oxygen from it, or in any way affecting its nature. Light does not act on dry chlorine; but if water be present, the chlorine decomposes that liquid, unites with the hydrogen to form hydrochloric acid, and oxygen gas is set at liberty. This change takes place quickly in sunshine, more slowly in diffused daylight, and not at all when light is wholly excluded. Hence the necessity of keeping moist chlorine gas, or its solution, in a dark place.

Chlorine unites with some substances with evolution of heat and light, and is hence termed a supporter of combustion. On plunging a lighted taper into chlorine gas, it burns for a short time with a small red flame, and emits a large quantity of smoke. Phosphorus takes fire in it spontaneously, and burns with a pale white light. Several of the metals, such as tin, copper, arsenic, antimony, and zinc, when introduced into chlorine in the state of powder or in fine leaves, are suddenly inflamed. In all these cases the combustible substances unite with chlorine.

Chlorine has a very powerful attraction for hydrogen; and many of the chemical phenomena to which it gives rise are owing to this property. A striking example is its power of decomposing water by the action of light, or at a red-heat; the same effect is produced on most compound substances, of which hydrogen is an element. For the same reason, when chlorine, water, and some other body which has a strong affinity for oxygen, are presented to one another, water is usually resolved into its elements, its hydrogen attaching itself to the chlorine, and its oxygen to the other body. Thus chlorine is, indirectly, one of the most powerful oxidizing agents which we possess.

When any compound of chlorine and an inflammable is exposed to the influence of galvanism, the inflammable body goes over to the —, and chlorine to the + pole of the battery. This establishes a close analogy between oxygen and chlorine, both of them being supporters of combustion, and both negative electrics.

Though formerly called an acid, it possesses no acid properties. It has not a sour taste, does not redden the blue colour of plants, and shows comparatively little disposition to unite with alkalies. Its strong affinity for the metals is sufficient to prove that it is not an acid; for chemists are not acquainted with any instance of an acid combining directly in definite proportion with a metal. Its action on the pure alkalies leads to complicated changes, which will be considered while speaking of the oxides of chlorine.

One of the most important properties of chlorine is its bleaching power. All animal and vegetable colours are speedily removed by chlorine; and when the colour is once discharged, it can never be restored. Davy proved that chlorine cannot bleach unless water is present. Thus dry litmus paper suffers no change in dry chlorine; but when water is admitted, the colour speedily disappears. It is well known also that hydrochloric acid is always generated when chlorine bleaches. From these facts it is inferred that water is decomposed during the process; that its hydrogen unites with chlorine, and that decomposition of the colouring matter is occasioned by the oxygen which is liberated. The bleaching property of binoxide of hydrogen and of chromic and permanganic acids, of which oxygen is certainly the decolorizing principle, leaves little doubt of the accuracy of the foregoing explanation.

Chlorine is useful, likewise, for the purposes of fumigation. The experience of Guyton-Morveau is sufficient evidence of its power in destroying the volatile principles given off by putrefying animal matter; it probably acts in a similar way on contagious effluvia. A peculiar compound, formed by the action of chlorine on soda, has been lately introduced for this purpose by Labarraque.

Chlorine is in general easily recognised by its colour and odour. Chemically it may be detected by its bleaching property, added to the circumstance that a solution of nitrate of oxide of silver occasions in it a dense white precipitate (a compound of chlorine and metallic silver), which becomes dark on exposure to light, is insoluble in acids, and dissolves completely in pure ammonia. The whole of the chlorine, however, is not thrown down; for the oxygen of the oxide of silver unites with a portion of chlorine, and converts it into chloric acid.

Those compounds of chlorine, which are not acid, are termed *chlorides* or *chlorurets*. The former expression, from the analogy between chlorine and oxygen, is perhaps the more appropriate.

Berzelius inferred the equivalent of chlorine from the oxygen lost by chlorate of potassa when decomposed by heat, and the quantity of chlorine found in the residual chloride of potassium. I investigated the same subject by examining into the composition of the nitrate of the oxide and chloride of silver, of the protoxide and chloride of lead, and of the peroxide and chlorides of mercury.

These researches concur in showing 36, the eq. of chlorine commonly adopted in this country, to be erroneous. The number inferred from the sp. gr. of chlorine and hydrogen gases is 35·84; but, unfortunately, the densities of these gases are not known with the precision required for an application of this nature.

Its eq. is 35·42; eq. vol. = 100; symb. Cl.

The composition of the compounds described in this section is as follows:—

	Chlorine.				Equiv.	Formulæ.
Hydrochloric Acid	35·42	1 eq.+ Hydrogen	1	1 eq. =	36·42	HCl.
Hypochlorous Acid	35·42	+ Oxygen	8	1 eq. =	43·42	ClO.
Chlorous Acid	35·42	+ Ditto	32	4 eq. =	67·42	ClO_4.
Chloric Acid	35·42	+ Ditto	40	5 eq. =	75·42	ClO_5.
Perchloric Acid	35·42	+ Ditto	56	7 eq. =	91·42	ClO_7.
Quadrochloride of Nitrogen	141·68	4 eq.+ Nitrogen	14·15	1 eq. =	155·83	NCl_4.
Protochloride of Carbon .	35·42	1 eq.+ Carbon	6·12	1 eq. =	41·54	CCl.
Dichloride of Carbon .	35·42	1 eq.+ Ditto	12·24	2 eq.=	47·66	C_2Cl.
Perchloride of Carbon .	106·26	3 eq.+ Carbon	12·24	2 eq. =	118·50	C_2Cl_3.
Dichloride of Sulphur	35·42	1 eq.+ Sulphur	32·2	2 eq. =	67·62	SCl.
Bichloride of Sulphur .	70	2 eq.+ Ditto	16·1	1 eq. =	86·1	SCl_2.
Sesquichloride of Phosphorus	106·26	3 eq.+ Phospho.	31·4	1 eq. =	137·66	P_2Cl_3.
Perchloride of Phosphorus	175	5 eq.+ Ditto	31·4	1 eq. =	206·4	P_2Cl_5.
Chlorocarbonic acid gas .	35·42	1 eq.+ Carb. ox.	14·12	1 eq. =	49·54	CO+Cl.
Terchloride of Boron . .	106·26	3 eq.+ Boron	10·9	1 eq. =	117·16	BCl_3.
Terchloride of Silicon . .	106·26	3 eq.+ Silicon	22·5	1 eq. =	128·76	$SiCl_3$.

Hydrochloric Acid.—Hist. and Prep.—A concentrated aqueous solution of this acid has been long known under the names of spirit of salt, and of marine or muriatic acid; but in its purer form of gas it was discovered in 1772 by Priestley. It may be conveniently prepared by putting an ounce of strong hydrochloric acid solution into a glass flask, and heating it by means of a lamp till the liquid boils, when the gas is freely evolved, and may be collected over mercury. Another method of preparing it is by the action of concentrated sulphuric acid on an equal weight of sea-salt. Brisk effervescence ensues at the moment of making the mixture, and on the application of heat a large quantity of hydrochloric acid gas is disengaged. In the former process, hydrochloric acid previously dissolved in water is simply expelled from the solution by heat. The explanation of the latter process is more complicated. Sea-salt was formerly supposed to be a compound of hydrochloric acid and soda; and, on this supposition, the soda was believed merely to quit the hydrochloric and unite with sulphuric acid. But the researches of Gay-Lussac, Thenard, and Davy, proved that it consists of chlorine and sodium combined in the ratio of their equivalents. The nature of its action with sulphuric acid will be understood by comparing the elements concerned in the change before and after it has occurred :—

Hydrous Sulp. Acid.			Chloride of Sodium.		Sulp. of Soda.			Hydrochloric Acid.	
Real Acid		40·1	Chlorine	35·42	Acid		40·1	Chlorine	35·42
Water	Hyd. Oxy.	1 8	Sodium	23·3	Soda	Sod. Oxy.	23·3 8	Hydrogen	1

or in symbols,

$$SO_3, HO+NaCl=SO_3, NaO+HCl.$$

Thus it appears that single equivalents of water, sulphuric acid, and chloride of sodium, yield sulphate of soda and hydrochloric acid. The water of the sulphuric acid is essential; so much so, indeed, that chloride of sodium is not decomposed at all by anhydrous sulphuric acid.

Hydrochloric acid may be generated by the direct union of its elements. When equal measures of chlorine and hydrogen are mixed together, and an electric spark is passed through the mixture, instantaneous combination takes place, heat and light are emitted, and hydrochloric acid is generated. A similar effect is produced by flame, by a red-hot body, and by spongy platinum. Light also causes them to unite. A mixture of the two gases may be preserved without change in a dark place; but if exposed to the diffused light of day, gradual combination ensues, which is completed in the course of 24 hours. The direct solar rays produce, like flame and electricity, sudden inflammation of the whole mixture, accompanied with explosion; and, according to Brande, the vivid light emitted by charcoal intensely heated by galvanic electricity acts in a similar manner.

This acid is most commonly used in the form of a concentrated aqueous solution, which is made by transmitting a current of the gas into water as long as any of it is absorbed. All the Pharmacopœias give directions for conducting the process. That adopted by the Edinburgh College is practically good. The proportions they recommend are equal weights of sea-salt, water, and sulphuric acid, more acid being purposely employed than is sufficient to form a neutral sulphate with the soda, so that the more perfect decomposition of the sea-salt may be insured. The acid, to prevent too violent effervescence at first, is mixed with one-third of the water; and when the mixture has cooled, it is poured upon the salt previously introduced into a glass retort. The distillation is continued to dryness; and the gas, as it escapes, is conducted into the remainder of the water. The theory of the process has been already explained. The residue is a mixture of sulphate and bisulphate of soda. The sp. gr. of the acid solution obtained by this process is 1·170.

Prop.—It is a colourless gas, has a pungent odour and an acid taste. Under a pressure of 40 atmospheres, and at the temperature of 50°, it is liquid. Sp. gr. 1·2695. It is quite irrespirable, exciting violent spasm of the glottis; but when diluted with air, it is far less irritating than chlorine. All burning bodies are extinguished by it, nor is the gas itself inflammable.

It is not chemically changed by mere heat. It is readily decomposed by galvanism, hydrogen appearing at the —, and chlorine at the + pole. It is also decomposed by ordinary electricity. The decomposition, however, is incomplete; for though one electric spark resolves a portion of the gas into its elements, the next shock in a great measure effects their reunion. It is not affected by oxygen under common circumstances; but if a mixture of oxygen and hydrochloric acid gases is electrified, the oxygen unites with the hydrogen of the acid to form water, and chlorine is set at liberty. For this and the preceding fact we are indebted to the researches of Henry.

One of the most striking properties of hydrochloric acid gas is its powerful attraction for water. A dense white cloud appears whenever it escapes into the air, owing to its combining with the aqueous vapour of the atmosphere. A piece of ice put into a jar full of the gas confined over mercury liquefies on the instant, and the whole of the gas disappears in the course of a few seconds. On opening a long wide jar of hydrochloric acid gas under water, the absorption of the gas takes place so instantaneously, that the water is forced up into the jar with the same violence as into a vacuum. Considerable increase of temperature takes place during the absorption, and therefore the apparatus should be kept cool by ice. Davy states (Elements, p. 252) that water at the temperature of 40° absorbs 480 times its volume of the gas, and that the solution has a sp. gr. of 1·2109. Thomson finds that one cubic inch of water at 69° absorbs 418 cubic inches of gas, and occupies the space of 1·34 cubic inch. The solution has a sp. gr. of 1·1958, and one cubic inch of it contains 311·04 cubic inches of hydrochloric acid gas. The quantity of real acid contained in solutions of different densities may be determined by ascertaining the quantity of pure marble dissolved by a given weight of each. Every 50·6 grains of marble correspond to 36·42 of real acid. The following table from Thomson's "Principles of Chemistry," is constructed according to this rule. The first and second columns show the atomic constitution of each acid.

Table exhibiting the Specific Gravity of Muriatic Acid of determinate Strengths.

Atoms of Acid.	Atoms of Water.	Real Acid in 100 of the liquid.	Specific Gravity.	Atoms of Acid.	Atoms of Water.	Real Acid in 100 of the liquid.	Specific Gravity.
1	6	40·659	1·203	1	14	22·700	1·1060
1	7	37·000	1·179	1	15	21·512	1·1008
1	8	33·945	1·162	1	16	20·442	1·0960
1	9	31·346	1·149	1	17	19·474	1·0902
1	10	29·134	1·139	1	18	18·590	1·0860
1	11	27·206	1·1285	1	19	17·790	1·0820
1	12	25·517	1·1197	1	20	17·051	1·0780
1	13	24·026	1·1127				

Hydrochloric acid of commerce has a yellow colour, and is always impure. Its usual impurities are nitric acid, sulphuric acid, and oxide of iron. The presence of nitric acid may be inferred if the hydrochloric acid has the property of dissolving gold leaf. Iron may be detected by ferrocyanuret of potassium, and sulphuric acid by chloride of barium, the suspected hydrochloric acid being previously diluted with three or four parts of water. The presence of nitric acid is provided against, by igniting the sea-salt, as recommended by the Edinburgh College, in order to decompose any nitre which it may contain. The other impurities may be avoided by employing Woulfe's Apparatus. A few drachms of water are put into the first bottle to retain the chloride of iron and sulphuric acid which pass over, and the hydrochloric acid gas is condensed in the second.

A strong solution of pure hydrochloric acid is a colourless liquid, which emits white vapours when exposed to the air, is intensely sour, reddens litmus paper strongly, and neutralizes alkalies. It combines with water in every proportion, and causes increase of temperature when mixed with it, though in a much less degree than sulphuric acid. It freezes at −60° F.; and boils at 110°, or a little higher, giving off pure hydrochloric acid gas in large quantity.

Hydrochloric acid is decomposed by substances which yield oxygen readily. Thus several peroxides, such as those of manganese, cobalt, and lead, effect its decomposition. Chloric, iodic, bromic, nitric, and selenic acids act on the same principle. A mixture of nitric and hydrochloric acids, in the ratio of one measure of the former to two of the latter, has long been known under the name of *Aqua regia*, as a solvent for gold and platinum. When these acids are mixed together, the solution instantly becomes yellow; and on heating the mixture, pure chlorine is evolved, and the colour of the solution deepens. On continuing the heat, chlorine and nitrous acid vapours are disengaged. At length the evolution of chlorine ceases, and the residual liquid is found to be a solution of hydrochloric and nitrous acids, which is incapable of dissolving gold. The explanation of these facts is, that nitric and hydrochloric acids decompose one another, giving rise to the production of water and nitrous acid, and the separation of chlorine; while hydrochloric and nitrous acids may be heated together without mutual decomposition. It is hence inferred that the power of nitro-hydrochloric acid in dissolving gold is owing to the chlorine which is liberated. (Davy in the Quarterly Journal, vol. i.)

Hydrochloric acid is distinguished by its odour, volatility, and strong acid properties. With nitrate of oxide of silver it yields the same precipitate as chlorine; but no chloric acid is generated, because the oxygen of the oxide of silver unites with the hydrogen of the hydrochloric acid, and the chlorine in consequence is entirely precipitated. Notwithstanding that nitrate of oxide of silver yields the same precipitate with chlorine and hydrochloric acid, there is no difficulty in distinguishing between them; for the bleaching property of the former is a sure ground of distinction.

The composition of hydrochloric acid has been determined by Davy, and Gay-Lussac and Thenard. Their experiments concur in proving that chlorine and hydrogen unite in equal volumes, and that the hydrochloric acid, which is the sole and constant product, occupies the same space as the gases from which it is formed. From these facts the composition of hydrochloric acid is easily inferred. For, as

	Grains.
50 cubic inches of Chloride weigh	38·299
50 ,, ,, of Hydrogen	1·0699
100 C. I. of Hydrochloric acid gas must weigh .	39·3689.

These numbers are in the ratio of 1 to 35·84, being nearly that of single eq. of hydrogen and chlorine. Hence its eq. is 36·42; eq. vol. = 100; symb. H + Cl, or HCl.

COMPOUNDS OF CHLORINE AND OXYGEN.

The leading character of these compounds is derived from the circumstance that chlorine and oxygen, the attraction of which for most elementary substances is so energetic, have but a feeble affinity for each other. These principles, consequently, are never met with in nature in a state of combination. Indeed, they cannot be made to combine directly; and when they do unite, very slight causes effect their separation. Chemists have long been doubtful as to the exact number of the compounds of chlorine and oxygen. The recent labours of Balard and Martens have established the existence of four, all of which they have shown to possess acid properties. Their names and constitutions are given in the subjoined table.

	By weight.		By volume.	
	Chl.	Oxy.	Chl.	Oxy.
Hypochlorous acid	35·42	8	2	1
Chlorous acid	35·42	32	2	4
Chloric acid	35·42	40	2	5
Perchloric acid	35·42	56	2	7

According to the practice of most British chemists, two volumes of chlorine, as also two volumes of hydrogen and of nitrogen, are considered as respectively corresponding to one equivalent or one atom; whereas one volume of oxygen corresponds to one equivalent. Berzelius with many Continental chemists, considering the atoms of all elements to possess the same volume, regard the four preceding compounds as composed of 2 atoms or 2 eqs. of chlorine combined with 1, 4, 5, and 7 atoms or eqs. of oxygen.

Hypochlorous Acid.—Hist. and Prep.—Davy, in 1811, discovered a gaseous compound, which was described by him in the Philosophical Transactions of the same year under the name of Euchlorine. This gas, which until recently has been considered to be the protoxide of chlorine, is made by the action of hydrochloric acid on the chlorate of potassa; and its production is explicable by the fact, that hydrochloric and chloric acids mutually decompose each other. When hydrochloric acid and chlorate of potassa are mixed together, more or less of the potassa is separated by the hydrochloric from the chloric acid, and the latter being set at liberty, reacts on free hydrochloric acid. The result depends upon the relative quantities of the materials. If hydrochloric acid be in excess, the chloric acid undergoes complete decomposition. For each eq. of chloric acid, 5 eq. of hydrochloric acid are decomposed: the 5 eq. of oxygen, contained in the former, unite with the hydrogen of the latter, producing 5 eq. of water; while the chlorine of both acids is disengaged. If, on the contrary, chlorate of potassa be in excess, the chloric acid is deprived of part of its oxygen only; the products are water and the euchlorine of Davy. The chloric and hydrochloric acids react on each other in the ratio of 1 eq. to 2, or what is the same thing, in that of 4 eq. to 8 eq.; thus

$$4ClO_5+8HCl=8HO+12ClO.$$

The gas thus obtained, though containing chlorine and oxygen in the ratio of atom to atom, is not, as was supposed by Davy, a distinct compound, but is a mixture of chlorine and chlorous acid. For this fact, which has long been suspected, we are indebted to the researches of Soubeiran. On transmitting a stream of euchlorine through a tube nearly full of calomel, the free chlorine is readily absorbed; on subsequently exploding the purified gas, he obtained one volume of chlorine to two volumes of oxygen, being the exact composition of chlorous acid. The product of the last decomposition is therefore

$$3ClO_4+9Cl, \text{ and not } 12ClO.$$

The experiments of Soubeiran have been confirmed by the discoveries of Balard.

If a stream of chlorine gas be passed into a solution of the pure alkalies, or be allowed to act upon the alkaline earths in the form of hydrates, a bleaching substance is procured which has been commonly viewed as a direct compound of chlorine and an alkaline base. It consists, however, according to Balard, of a mixture of a metallic chloride and the hypochlorite of the alkali employed (An. de Ch. et Ph. lvii. 225). The process recommended for obtaining the pure acid is to pour into bottles filled with chlorine gas peroxide of mercury in fine powder, and mixed with twice its weight of distilled water: by brisk agitation the chlorine is rapidly and completely absorbed, if a slight excess of the peroxide be used. By this process one portion of the peroxide of mercury, $Hg\ O_2$, is decomposed, both its constituents combining with chlorine, the mercury forming corrosive sublimate, $Hg\ Cl_2$, and the oxygen hypochlorous acid. The latter remains in solution in the water; while the former, by combining with undecomposed peroxide of mercury, forms the sparingly soluble oxychloride of mercury, which is separated by filtration. The hypochlorous acid being volatile, is obtained in a pure but diluted state by distillation. The temperature which is used for this purpose should be kept considerably below 212°, as the hypochlorous acid decomposes rapidly at that heat: the process is, therefore, best performed under reduced pressure. A more concentrated solution of the acid is obtained by submitting the first products to a second distillation.

Prop.—As thus obtained, hypochlorous acid is a transparent liquid of a slightly yellow colour when concentrated. Its odour is strong and penetrating, and different though somewhat similar to chlorine. Its action on the skin is exceedingly active, the effect being similar to but greater than that produced by nitric acid. It is a highly bleaching compound. In a concentrated state it is very unstable, a slow decomposition taking place at common temperatures, by which chlorine is evolved and chloric acid produced. This change is promoted by light, and is effected almost instantly by exposure for a few moments to the direct rays of the sun. It is also decomposed by agitation with angular bodies; and on throwing into the acid a portion of pounded glass, a brisk effervescence is observed from the escape of chlorine.

It is one of the most powerful oxidizing agents. Its action in this respect, however, is various, and is principally observed in relation to the simple non-metallic elements. Thus sulphur and phosphorus are readily brought to their highest state of oxidation, and even selenium is converted into selenic acid, an effect which the nitric acid cannot accomplish. Iodine and bromine are also instantly changed into iodic and bromic acids. Its action on the more perfect metals, on the contrary, is slight: iron and silver, however, are remarkable exceptions to this rule; for when either of them is brought in a finely divided state in contact with hypochlorous acid, the latter suffers instantaneous decomposition. When iron is used, it is oxidized at the expense of the acid, and chlorine is evolved; with silver the oxygen escapes, and the chlorine unites exclusively with the metal. The decomposition of hypochlorous acid may also be produced by metallic mercury, but the decomposition is unattended by the evolution of either gas. Both the chloride and oxide of mercury are produced, and instantly unite to form the oxychloride.

Balard has also succeeded in obtaining hypochlorous acid in the gaseous form. A small quantity of a concentrated solution is introduced into a bell jar over mercury, and fragments of dry nitrate of lime are successively added. The nitrate of lime being highly deliquescent, unites with the water, and the acid gas escapes with effervescence: the presence of the saline solution is essential, as it prevents the decomposition of the gas by the mercury. The gas is of a yellowish green colour, and is very similar to chlorine in appearance. It unites rapidly by water, which absorbs at least 100 times its own volume of gas. It detonates by a slight increase of temperature; and though less explosive than the chlorous acid, there is a probability of an accident in transferring it from one vessel to another. The results of explosion are oxygen and chlorine; and Balard found that 100 measures produced 100 of chlorine and 50 of oxygen. From these data its sp. gr. is 3·0212; its eq. 43·42; eq. vol. = 100; symb. $\text{Cl} + \text{O}$, $\dot{\text{Cl}}$ or ClO.

Chlorous Acid.—Hist. and Prep.—This compound was discovered by Davy in 1815 (Phil. Trans.), and soon after by Count Stadion of Vienna. It is formed by the action of sulphuric acid on chlorate of potassa. A quantity of this salt, not exceeding 50 or 60 grains, is reduced to powder, and made into a paste by the addition of strong sulphuric acid. The mixture, which acquires a deep yellow colour, is placed in a glass retort, and heated by warm water, the temperature of which is kept under 212° F. A bright yellowish green gas of a richer colour than chlorine is disengaged, which has an aromatic odour without any smell of chlorine, is absorbed rapidly by water, to which it communicates its tint. This gas, which has long been described as the peroxide of chlorine, must now be called chlorous acid, as it has been shown to possess acid properties, and to form definite compounds with the alkaline bases.

The chemical changes which take place in the process are explained in the following manner. The sulphuric acid decomposes some of the chlorate of potassa, and sets chloric acid at liberty. The chloric acid, at the moment of separation, resolves itself into peroxide of chlorine and oxygen; the last of which, instead of escaping as free oxygen gas, goes over to the acid of some undecomposed chlorate of potassa, and converts it into perchloric acid. The products are bisulphate and perchlorate of potassa, and chlorous acid. It is most probable, from the data contained in the preceding table, that every 3 eq. of chloric acid yield 1 eq. of perchloric acid and 2 eq. of chlorous acid.

Prop.—Chlorous acid unites readily with the alkalies and alkaline earth, forming salts which are more stable than those of the hypochlorous acid. They are produced by transmitting the gas into the alkaline solutions, which may thus be rendered perfectly neutral (Martens, An. de Ch. et Ph. lxi. 293). All the salts hitherto examined are soluble in water, and are possessed, like the acid itself, of bleaching properties. The neutral salts pass readily into a metallic chloride and chlorate of the base, particularly such as the chloride of potash, which form a sparingly soluble chlorate. This change does not so readily ensue when alkali is in excess. The proportion in which the chloride and chlorate are produced indicate that 6 eq. of chlorite are decomposed, by which 1 eq. of metallic chloride and 5 eq. of chlorate are produced: thus $6KO\,ClO_4$ yields KCl and $5KO\,ClO_5$. The solution of the pure acid gradually yields chloric acid and chlorine. It is a powerful oxidizing agent, and in this respect is very similar to the hypochlorous acid. It causes a precipitate with nitrate of silver; but it is best recognized by the evolution of chlorous acid gas on the addition of an acid to its salts.

Phosphorus takes fire when introduced into the gas, and occasions an explosion. It explodes violently when heated to a temperature of 212°, emits a strong light, and undergoes a greater expansion than protoxide of chlorine. According to Davy, whose result is confirmed by Gay-Lussac, 40 measures of the gas occupy after explosion the space of 60 measures; and of these, 20 are chlorine and 40 oxygen. The peroxide is therefore composed of 35·42 parts, or 1 eq. of chlorine, united with 32 or 4 eq. of oxygen; and its sp. gr. must be 23·375.

Its eq. is 67·42; eq. vol. = 100; symb. $Cl + 4O$, $\overset{\cdot\cdot\cdot\cdot}{Cl}$, or ClO_4.

Chloric Acid.—Prep.—If a current of chlorine gas be transmitted into a strong solution of pure potassa, a portion of the alkali is decomposed, and chloride of potassium and hypochlorite of potassa are generated. On bringing the solution to the boiling point, the latter salt is decomposed. The changes which occur are complicated, and give rise to the evolution of oxygen, and the formation of chlorate of potassa and chloride of potassium. According to the experiments of Morin and Soubeiran, which accord entirely with the observations of Balard, 9 eq. of hypochlorite of potassa produce 1 eq. of chlorate of potassa, 8 eq. of chloride of potassium, and 12 eq. of oxygen: or thus,

$$9(KO+ClO) \text{ yield } (KO+Clo_5),\ 8KCl, \text{ and } 12O.$$

Hence for every eq. of chlorate, 17 eq. of chloride are formed.

When to a dilute solution of chlorate of baryta a quantity of weak sulphuric acid, exactly sufficient for combining with the baryta, is added, the insoluble sulphate of baryta subsides, and pure chloric acid remains in the liquid. This acid, the existence of which was originally observed by Mr. Chenevix, was first obtained in a separate state by Gay-Lussac.

Prop.—Chloric acid reddens vegetable blue colours, has a sour taste, and forms neutral salts, called *chlorates* (formerly *hyperoxymuriates*), with alkaline bases. It possesses no bleaching properties, a circumstance by which it is distinguished from chlorine, hypochlorous, and chlorous acids. It gives no precipitate in solution of nitrate of oxide of silver, and hence cannot be mistaken for hydrochloric acid. Its solution may be concentrated by gentle heat till it acquires an oily consistence without decomposition: in this state of highest concentration it acquires a yellowish tint, emits an odour of nitric acid, sets fire to paper and other dry organic matter, and converts alcohol into acetic acid. When sharply heated in a retort, part of the acid is resolved into chlorine and oxygen; but another portion, acquiring oxygen from that which is decomposed, is converted into perchloric acid, and then passes over into the receiver in the form of a dense colourless liquid (Serullas). Chloric acid is easily decomposed by deoxidizing agents. Sulphurous acid, for instance, deprives it of oxygen, with formation of sulphuric acid and evolution of chlorine. By the action of hydrosulphuric acid, water is generated, while sulphur and chlorine are set free. The power of hydrochloric acid in effecting its decomposition has already been explained.

Chloric acid is readily known by forming a salt with potassa, which crystallizes in tables and has a pearly lustre, deflagrates like nitre when flung on burning charcoal, and yields peroxide of chlorine by the action of concentrated sulphuric acid. Chlorate of potassa, like most of the chlorates, gives off pure oxygen when heated to redness, and leaves a residue of chloride of potassium. By this mode Gay-Lussac ascertained the composition of chloric acid, as stated in the preceding table. (An. de Chimie, xci.)

Its eq. is 75·42; symb. $Cl + 5O$, $\overset{\cdot\cdot\cdot\cdot\cdot}{Cl}$, or ClO_5.

Perchloric Acid.—The saline matter which remains in the retort after forming chlorous acid, is a mixture of perchlorate and bisulphate of potassa; and by washing it with cold water, the bisulphate is dissolved, and the perchlorate is left. Perchloric acid may be prepared from this salt by mixing it in a retort with half its weight of sulphuric acid, diluted with one-third of water, and applying heat to the mixture. At the temperature of about 284° F. white vapours rise, which condense as a colourless liquid in the receiver. This is a solution of perchloric acid.

The existence of perchloric acid was first ascertained by Count Stadion, who found it to be a compound of 2 volumes or 1 eq. of chlorine and 7 of oxygen; and this view of its constitution has been confirmed by Gay-Lussac, Serullas, and Mitscherlich. (An. de Ch. et Ph. viii. ix. xlvi. 297, and xlix. 113.) According to Serullas, it is a very stable compound: it may be heated with hydrochloric or sulphuric acid without change, does not set fire to organic substances, and is not decomposed by alcohol. When concentrated it has a density of 1·65, in which state it emits vapour when exposed to the air, absorbs hygrometric moisture powerfully, and boils at 392° F. By admixture with strong sulphuric acid and distilling, Serullas obtained it in the solid form, both massive and in elongated prisms. It hisses when thrown into water, like red-hot iron when quenched.

Of all the salts of perchloric acid, that with potassa is the most insoluble, requiring 65 times its weight of water at 60° for solution. This salt is readily and safely formed by adding chlorate of potassa, well dried and in fine powder, in small portions at a time, to an equal weight of concentrated sulphuric acid, gently warmed in an open vessel. The chlorous acid gas escapes without danger, and the chlorate is entirely converted into perchlorate and bisulphate of potassa, the latter of which, being very soluble, is easily removed by cold water. Serullas finds that chlorate of potassa, when decomposed by a low heat, is converted into chloride of potassium and perchlorate of potassa; but the temperature must be carefully managed, otherwise the perchlorate itself would be resolved into oxygen and chloride of potassium. The perchlorate thus procured is purified by solution in hot water and crystallization. It is distinguished from chlorate of potassa by not acquiring a yellow tint on the addition of hydrochloric acid. The primary form of its crystals, according to Mitscherlich, is a right rhomboidal prism isomorphous with permanganate of potassa.

Its eq. is 91·42; symb. $Cl + 7O$, $\overset{\cdot\cdot\cdot\cdot\cdot\cdot\cdot}{Cl}$, or ClO_7.

Quadrochloride of Nitrogen.—*Hist. and Prep.*—This compound was discovered by Dulong in 1811. It elements have a feeble mutual affinity, and do not unite when presented to each other in their gaseous form. The condition which leads to their union is the decomposition of ammonia by chlorine, during which hydrochloric acid is generated by chlorine combining with the hydrogen of ammonia; while the nitrogen of that alkali, in its nascent state, enters into combination with another portion of chlorine. A convenient mode of preparing the quadrochloride of nitrogen is the following. An ounce of hydrochlorate of ammonia is dissolved in 12 or 16 ounces of hot water; and when the solution has cooled to the temperature of 90°, a glass bottle with a wide mouth, full of chlorine, is inverted in it. The solution gradually absorbs the chlorine, and acquires a yellow colour; and in about 20 minutes globules of a yellow fluid are seen floating like oil upon its surface, which, after acquiring the size of a small pea, sink to the bottom of the liquid. The drops of the chloride, as they descend, should be collected in a small saucer of lead, placed for that purpose under the mouth of the bottle. It is also readily obtained by suspending a fragment of sal-ammonia in a solution of hypochlorous acid.

Prop.—It is one of the most explosive compounds yet known, having been the cause of serious accidents both to its discoverer and to Davy. (Phil. Trans. 1813; An. de Ch. lxxxvi.) Its specific gravity is 1·653. It does not congeal in the intense cold produced by a mixture of snow and salt. It may be distilled at 160°; but at a temperature between 200° and 212° it explodes. It appears from the investigation of Messrs. Porrett, Wilson, and Kirk, that its mere contact with some substances of a combustible nature causes detonation even at common temperatures. This result ensues particularly with oils, both volatile and fixed. I have never known olive oil fail in producing the effect. The products of the explosion are chlorine and nitrogen. (Nicholson's Journal, xxxiv.)

Sir H. Davy analyzed chloride of nitrogen by means of mercury, which unites with chlorine, and liberates the nitrogen. He inferred from his analysis that its elements are united in the proportion of four measures of chlorine to one of nitrogen; and it hence follows that, by weight, it consists of 4 eq. of chlorine and 1 eq. of nitrogen.

Perchloride of Carbon. — *Hist. and Prep.* — The discovery of this compound is due to Mr. Faraday. When olefiant gas (a compound of carbon and hydrogen) is mixed with chlorine, combination takes place between them, and an oil-like liquid is generated, which consists of chlorine, carbon, and hydrogen. On exposing this liquid in a vessel full of chlorine gas to the direct solar rays, the chlorine acts upon and decomposes the liquid, hydrochloric acid is set free, and the carbon, at the moment of separation, unites with the chlorine. (Phil. Trans. 1821.)

Prop.—Perchloride of carbon is solid at common temperatures, has an aromatic odour approaching to that of camphor, is a non-conductor of electricity, and refracts light very powerfully. Its sp. gr. is exactly double that of water. It fuses at 320°, and after fusion it is colourless and very transparent. It boils at 360°, and may be distilled without change, assuming a crystalline arrangement as it condenses. It is sparingly soluble in water, but dissolves in alcohol and ether, especially by the aid of heat. It is soluble also in fixed and volatile oils.

It burns with a red light when held in the flame of a spirit-lamp, giving out acid vapours and smoke; but the combustion ceases as soon as it is withdrawn. It burns vividly in oxygen gas. Alkalies do not act upon it; nor is it changed by the stronger acids, such as the hydrochloric, nitric, or sulphuric acids, even with the aid of heat. When its vapour, mixed with hydrogen, is transmitted through a red-hot tube, charcoal is separated, and hydrochloric acid gas evolved. On passing its vapour over the peroxides of metals, such as that of mercury and copper, heated to redness, a chloride of the metal and carbonic acid are generated. Protoxides, under the same treatment, yield carbonic oxide gas and metallic chlorides. Most of the metals decompose it also at the temperature of ignition, uniting with its chlorine, and causing deposition of charcoal.

The composition of the perchloride of carbon was inferred by Faraday from the proportions of chlorine and olefiant gas employed in its production, and from the quantity of chloride of copper and carbonic acid generated when its vapour was transmitted over oxide of copper at a red heat.

Its eq. is 118·50; symb. $2C + 3Cl$, or $C_2\ Cl_3$.

Protochloride of Carbon.—When the vapour of the perchloride is passed through a red-hot glass or porcelain tube, filled with fragments of rock crystal to increase the quantity of heated surface, partial decomposition occurs, chlorine gas escapes, and a vapour which, analyzed by Faraday by means of oxide of copper, proved to be protochloride of carbon. At common temperatures it is a limpid colourless liquid, which has a density of 1·5526, does not congeal at 0° F., and at 160° or 170° is converted into vapour. It may be distilled repeatedly without change; but when exposed to a red heat, some of it is resolved into its elements. In its chemical relations it is very analogous to perchloride of carbon.

Its eq. is 41·54; symb. $C + Cl$, or $C\,Cl$.

Dichloride of Carbon.—The first sample of this substance yet obtained was brought from Sweden by M. Julin, and is said to have been formed during the distillation of nitric acid from crude nitre and sulphate of iron. It occurs in small, soft, adhesive fibres of a white colour, which have a peculiar odour, somewhat resembling spermaceti. It fuses on the application of heat, and boils at a temperature between 350° and 450° F. At 250° it sublimes slowly, and condenses again in the form of long needles. It is insoluble in water, acids, and alkalies; but is dissolved by hot oil of turpentine or by alcohol, and forms acicular crystals as the solution cools. It burns with a red flame, emitting much smoke and fumes of hydrochloric acid gas. It has since been obtained among the products of the action of chlorine, aided by light, on some organic compounds.

The nature of this substance is shown by the following circumstances. When its vapour is exposed to a red heat, evolution of chlorine gas ensues, and charcoal is deposited. A similar deposition of charcoal is produced by heating it with phosphorus, iron, or tin; and a chloride is formed at the same time. Potassium burns vividly in its vapour with formation of chloride of potassium and separation of charcoal. On detonating a mixture of its vapour with oxygen gas over mercury, a chloride of that metal and carbonic acid are generated. By these means Phillips and Faraday ascertained its composition (An. of Phil. xviii. 150). Its eq. is 47·66; symb. $2C + Cl$, or $C_2\,Cl$.

Dichloride of Sulphur.—This compound was discovered in the year 1804 by Thomson,[*] and was afterwards examined by Berthollet.[†] It is most conveniently prepared by passing a current of chlorine gas over flowers of sulphur gently heated, until nearly all the sulphur disappears. Direct combination ensues, and the product, distilled off from uncombined sulphur, is obtained under the form of a liquid which appears red by reflected, and yellowish green by transmitted light. Its density is 1·687. It is volatile below 200°, boils at 280°, yielding vapour which has a density of 4·70, and condenses again without change in cooling. When exposed to the air it emits acrid fumes, which irritate the eyes powerfully, and have an odour somewhat resembling sea-weed, but much stronger. Dry litmus paper is not reddened by it, nor does it unite with alkalies. It acts with energy on water: — mutual decomposition ensues, with formation of hydrochloric and hyposulphurous acids, and deposite of sulphur, by which the water is rendered cloudy. From a recent analysis by Rose it consists of 35·42 parts or 1 eq. of chlorine and 32·2 parts or 2 eq. of sulphur (Pog. An. xxi. 431).

---

[*] Nicholson's Journal, vol. vi.

[†] Mémoires d'Arcueil, vol. i.

Its eq. is 67·62; symb. $2S + Cl$, or $S_2 Cl$.

Rose maintains that the preceding is the only chloride of sulphur, arguing that the chloride analyzed by Davy was merely dichloride of sulphur holding chlorine in solution. Dumas, on the other hand, contends, that when sulphur is acted on by excess of chlorine, a chloride of sulphur is really obtained, which is apt to retain traces of the dichloride, and can only be purified by repeated distillation at about 140° F. This chloride is a liquid of a deep reddish brown tint, and has a density of 1·62. It boils at 147°, and the density of its vapour is between 3·67 and 3·70. By decomposition in water it should yield hydrochloric and hyposulphurous acids. (An. de Ch. et Ph. xlix. 205.)

Perchloride of Phosphorus.—There are two definite compounds of chlorine and phosphorus, the nature of which was first satisfactorily explained by Davy (Elements, p. 290). When phosphorus is introduced into a jar of dry chlorine, it inflames, and on the inside of the vessel a white matter collects, which is *perchloride of phosphorus*. It is very volatile, a temperature much below 212° being sufficient to convert it into vapour. Under pressure it may be fused, and it yields transparent prismatic crystals in cooling.

Water and perchloride of phosphorus mutually decompose each other; and the sole products are hydrochloric and phosphoric acids. Now in order that these products should be formed, consistently with the constitution of phosphoric acid, as stated at page 259, the perchloride must consist of 31·4 parts or 2 eq. of phosphorus, and 177·1 parts or 5 eq. of chlorine. One equivalent of the chloride and 5 eq. of water will then mutually decompose each other without any element being in excess, and yield 1 eq. of phosphoric, and 5 eq. of hydrochloric acid. This proportion is not far from the truth; for, according to Davy, one grain of phosphorus is united in the perchloride with six of chlorine.

Its eq. is 206·4; symb. $2P + 5Cl$, or $P_2 Cl_5$.

Sesquichloride of Phosphorus may be made either by heating the perchloride with phosphorus, or by passing the vapour of phosphorus over corrosive sublimate contained in a glass tube. It is a clear liquid like water, of sp. gr. 1·45; emits acid fumes when exposed to the air, owing to the decomposition of watery vapour; but when pure it does not redden dry litmus paper. On mixing it with water, mutual decomposition ensues, heat is evolved, and a solution of hydrochloric and phosphorous acids is obtained. It hence appears to consist of 31·4 parts or 2. eq. of phosphorus, and 106·26 parts or 3 eq. of chlorine. Its eq. is 137·66; symb. $2P + 3Cl$, or P_2Cl_3.

When hydrosulphuric acid gas is transmitted through a vessel containing perchloride of phosphorus, hydrochloric acid is disengaged, and a liquid produced which, according to Serullas, is a compound of three equivalents of chlorine, one of phosphorus, and one of sulphur. (An. de Ch. et Ph. xlii. 25.)

Chlorocarbonic Acid Gas.—Hist. and Prep.—This compound was discovered in 1812 by John Davy, who described it in the Philosophical Transactions for that year, under the name of *phosgene gas.* (From *φως light*, and *γεννασειν to produce.*) It is made by exposing a mixture of equal measures of dry chlorine and carbonic oxide gases to sunshine, when rapid but silent combination ensues, and they contract to one half their volume. Diffused day-light also effects their union slowly; but they do not combine at all when the mixture is wholly excluded from light.

Prop.—It is colourless gas, has a strong odour, and reddens dry litmus paper. It combines with four times its volume of ammoniacal gas, forming a white solid salt; so that it possesses the characteristic property of acids. It is decomposed by contact with water. One equivalent of each compound undergoes decomposition; and as the hydrogen of the water unites with chlorine, and its oxygen with carbonic oxide, the products are carbonic and hydrochloric acids. When tin is heated in this gas, chloride of tin is generated, and carbonic oxide gas set free, which occupies exactly the same space as the chlorocarbonic acid which was employed. A similar change occurs when it is heated in contact with antimony, zinc, or arsenic.

As chlorocarbonic acid gas contains its own volume of each of its constituents, it follows that 100 cubic inches of that gas at the standard temperature and pressure must weigh 106·806 grains; namely, 76·599 of chlorine added to 30·207 of carbonic oxide. Its sp. gr. is therefore 3·4427, and it consists of 35·42 parts or 1 eq. of chlorine, and 14·15 parts or 1 eq. of carbonic oxide.

Its eq. is 49·54; symb. $C + O + Cl$, or $CO\,Cl$.

Terchloride of Boron.—Davy noticed that recently prepared boron takes fire spontaneously in an atmosphere of chlorine, and emits a vivid light; but he did not examine the product. Berzelius remarked, that if the boron has been previously heated, whereby it is rendered more compact, the combustion does not take place till heat is applied. This observation led him to expose boron, thus rendered dense, in a glass tube to a current of dry chlorine; and to heat it gently as soon as the atmospheric air was completely expelled, in order to commence the combustion. The resulting compound proved to be a colourless gas; and on collecting it over mercury, which absorbed free chlorine, he procured the chloride of boron in a state of purity. This gas is rapidly absorbed by water; but double decomposition takes place at the same instant, giving rise to hydrochloric and boracic acids as the sole products: from this fact is inferred the composition of the chloride; for 1 eq. of terchloride of boron or $B + 3\,Cl$, and 3 eq. of water or $3(H + O)$, correspond to 1 eq. of boracic acid or $B + 3O$, and 3 eq. of hydrochloric acid or $3(H + Cl)$. The watery vapour of the atmosphere occasions a similar change; so that when the gas is mixed with air containing hygrometric moisture, a dense white cloud is produced. The sp. gr. of the gas, according to Dumas, is 3·942. It is soluble in alcohol, and communicates to it an ethereal odour, apparently by the action of hydrochloric acid. It unites with ammoniacal gas, forming a fluid volatile substance, the nature of which is unknown. —(Annals of Phil. xxvi. 129.)

Dumas finds that chloride of boron may be generated by the action of dry chlorine on a mixture of charcoal and boracic acid, heated to redness in a porcelain tube. Although neither charcoal nor chlorine can, when acting alone, decompose boracic acid, they do so readily by their united effort. According to Dumas, two volumes of chloride of boron, and three of carbonic oxide gas are formed. From these data chloride of boron may be considered as composed of 3 eq. vol. of chlorine and 1 eq. vol. of boron condensed into two volumes. Its sp. gr. is 4·079 (Dumas).

Despretz also appears to have invented a similar process. (Philos. Magazine and Annals, i. 469.)

Its eq. is 117·16; eq. vol. = 200; symb. $B + 3Cl$, or BCl_3.

Terchloride of Silicon.—When silicon is heated in a current of chlorine gas, it takes fire, and is rapidly volatilized. The product of the combustion condenses into a liquid, which appears to be naturally colourless, but to which an excess of chlorine communicates a yellow tint. This fluid is very limpid and volatile, and evaporates almost instantaneously in open vessels in the form of a white vapour. It boils at 124°, and bears a cold of zero without becoming solid. It has a suffocating odour not unlike that of cyanogen, and when put into water is converted into hydrochloric and silicic acids, the latter being easily obtained in a gelatinous form (Berzelius).

It may also be prepared by the method proposed by Oersted, which has been so successfully applied in the formation of other chlorides. It consists in mixing about equal parts of hydrated silicic acid and starch into a paste with oil, heating the mass in a covered crucible so as to char the starch, introducing the mixture in fragments into a porcelain tube, and then transmitting through it a current of dry chlorine gas while the tube is kept at a red heat. The chlorine unites with silicium, while the charcoal and oxygen combine. The volatile chloride is then agitated with mercury to separate the free chlorine, and purified by distillation.

Its eq. is 128·76; symb. $Si + 3Cl$, or $Si\,Cl_3$.

Chloro-nitrous Gas.—When fused chloride of sodium, potassium, or calcium, in powder, is treated with as much strong nitric acid as is sufficient to wet it, mutual decomposition ensues, and a new gas, composed of chlorine and binoxide of nitrogen, is generated. Its discoverer, Mr. E. Davy, describes it as a gas of a pale reddish yellow colour, of an odour similar to that of chlorine, though less pungent, and possessed of bleaching properties. It fumes on exposure to the air, and is freely absorbed by water. It is decomposed by sulphur, phosphorus, mercury, and most metals, and by substances in general which have an affinity for chlorine. It consists, according to Davy, of equal volumes of chlorine and binoxide of nitrogen, united without any condensation.

In the mutual decomposition of chloride of sodium and nitric acid, the products appear to be chloro-nitrous and chlorine gases, and nitrate of soda. Their formation must obviously depend on sodium being oxidized at the expense of nitric acid, while part of the chlorine unites, at the moment of separation from the sodium, with binoxide of nitrogen. (Phil. Mag. ix. 355.) Theoretically, it should be mixed with twice its volume of chlorine, the presence of which must materially obscure the properties of the new gas.

ON THE NATURE OF CHLORINE.

The change of opinion which has gradually taken place among chemists concerning the nature of chlorine, is a remarkable fact in the history of the science. The hypothesis of Berthollet, unfounded as it is, prevailed at one time universally. It explained phenomena so satisfactorily, and in a manner so consistent with the received chemical doctrine, that for some years no one thought of calling its correctness into question. A singular reverse, however, has taken place; and this hypothesis, though it has not hitherto been rigidly demonstrated to be erroneous, has within a short period been generally abandoned, even by persons who, from having adopted it in early life, were prejudiced in its favour. The reason of this will readily appear on comparing it with the opposite theory, and examining the evidence in favour of each.

Chlorine, according to the new theory, is maintained to be a simple body, because, like oxygen, hydrogen, and other analogous substances, it cannot be resolved into more simple parts. It does not indeed follow that a body is simple because it has not hitherto been decomposed; but as chemists have no other mode of estimating the elementary nature of bodies, they must necessarily adopt this one, or have none at all. Hydrochloric acid, by the same rule, is considered to be a compound of chlorine and hydrogen. For when exposed to the agency of galvanism, it is resolved into these substances; and by mixing the two gases in due proportion, and passing an electric spark through the mixture, hydrochloric acid gas is the product. Chemists have no other kind of proof of the composition of water, of potassa, or of any other compound.

Very different is the evidence in support of the theory of Berthollet. According to that view, hydrochloric acid gas is composed of *absolute muriatic acid* and water or its elements; chlorine consists of *absolute muriatic acid* and oxygen; and *absolute muriatic acid* is a compound of a certain unknown base and oxygen gas. Now all these propositions are gratuitous. For, in the first place, hydrochloric acid gas has not been proved to contain water. Secondly, the assertion that chlorine contains oxygen is opposed to direct experiment, the most powerful deoxidizing agents having been unable to elicit from that gas a particle of oxygen. Thirdly, the existence of such a substance as *absolute muriatic acid* is wholly without proof, and therefore its supposed base is also imaginary.

But this is not the only weak point of the doctrine. Since chlorine is admitted by this theory to contain oxygen, it was necessary to explain how it happens that no oxygen can be separated from it. For instance, on exposing chlorine to a powerful galvanic battery, oxygen gas does not appear at the positive pole, as occurs when other oxidized bodies are subjected to its action ; nor is carbonic acid or carbonic oxide evolved, when chlorine is conducted over ignited charcoal. To account for the oxygen not appearing under these circumstances, it was assumed that *absolute muriatic acid* is unable to exist in an uncombined state, and therefore cannot be separated from one substance except by uniting with another. This supposition was thought to be supported by the analogy of certain compounds, such as nitric and oxalic acids, which appear to be incapable of existing except when combined with water or some other substance. The analogy, however, is incomplete ; for the decomposition of such compounds, when an attempt is made to procure them in an insulated state, is manifestly owing to the tendency of their elements to enter into new combinations.

Admitting the various assumptions which have been stated, most of the phenomena receive as consistent an explanation by the old as by the new theory. Thus, when hydrochloric acid gas is resolved by galvanism into chlorine and hydrogen, it may be supposed that *absolute muriatic acid* attaches itself to the oxygen of the water, and forms chlorine ; while the hydrogen of the water goes to the opposite pole of the battery. When chlorine and hydrogen enter into combination, the oxygen of the former may be said to unite with the latter ; and that hydrochloric acid gas is generated by the water so formed combining with the *absolute muriatic acid* of the chlorine. The evolution of chlorine, which ensues on mixing hydrochloric acid and peroxide of manganese, is explained on the supposition that *absolute muriatic acid* unites directly with the oxygen of the black oxide of manganese.

It will not be difficult, after these observations, to account for the preference shown to the new theory. In an exact science, such as chemistry, every step of which is required to be matter of demonstration, there is no room to hesitate between two modes of reasoning, one of which is hypothetical, and the other founded on experiment. Nor is there, in the present instance, temptation to deviate from the strict logic of the science ; for there is not a single phenomenon which may not be fully explained on the new theory, in a manner quite consistent with the laws of chemical action in general.

It was supposed, indeed, at one time, that the sudden decomposition of water, occasioned by the action of that liquid on the compounds of chlorine with some simple substances, constitutes a real objection to the doctrine; but it will afterwards appear, that the acquisition of new facts has deprived this argument of all its force. While nothing therefore can be gained, much may be lost by adopting the doctrine of Berthollet. If chlorine is regarded as a compound body, the same opinion, though in direct opposition to the result of observation, ought to be extended to iodine and bromine; and as other analogous substances may hereafter be discovered, in regard to which a similar hypothesis will apply, it is obvious that this view, if proper in one case, may legitimately be extended to others. One encroachment on the method of strict induction would consequently open the way to another, and thus the genius of the science would eventually be destroyed.

An able attempt was made some years ago by the late Dr. Murray, to demonstrate the presence of water or its elements as a constituent part of hydrochloric acid gas, and thus to establish the old theory to the subversion of the new. The arguments which he used, though plausible and ingenious, were successfully combated by Sir H. and Dr. Davy. The only experiment which strictly bears upon the question — that, namely, where hydrochloric acid and ammoniacal gases were mixed together, goes far to demonstrate the absence of combined water in hydrochloric acid gas, and thereby to establish the views of Davy.*

SECTION XIII.

IODINE.

Hist.—Iodine was discovered in the year 1812 by M. Courtois, a manufacturer of saltpetre at Paris. In preparing carbonate of soda from the ashes of sea-weeds, he observed that the residual liquor corroded metallic vessels powerfully; and on investigating the cause of the corrosion, he noticed that sulphuric acid threw down a dark-coloured matter, which was converted by the application of heat into a beautiful violet vapour. Struck with its appearance, he gave some of the substance to M. Clément, who recognised it as a new body, and in 1813 described some of its leading properties in the Royal Institute of France. Its real nature was soon after determined by Gay-Lussac and Davy, each of whom proved that it is a simple non-metallic substance, exceedingly analogous to chlorine.*

---

* In Nicholson's Journal, vols. xxxi. xxxii. and xxxiv. Edinburgh Philos. Trans. vol. viii. and Philos. Trans. for 1818.

Iodine is frequently met with in nature in combination with potassium or sodium. Under this form it occurs in many salt and other mineral springs, both in England and on the Continent. It has been detected in the water of the Mediterranean, in the oyster and some other marine molluscous animals, in sponges, and in most kinds of sea-weed. In some of these productions, such as the *Fucus serratus* and *Fucus digitatus*, it exists ready formed, and according to Fyfe (Edin. Philos. Journal, i. 254) may be separated by the action of water; but in others it can be detected only after incineration. Marine animals and plants doubtless derive from the sea the iodine which they contain. Vauquelin found it also in the mineral kingdom, in combination with silver. (An. de Ch. et Ph. xxix.)

Prep.—The iodine of commerce is procured from the impure carbonate of soda, called kelp, which is prepared in large quantity on the northern shores of Scotland, by incinerating sea-weeds. The kelp is employed by soap-makers for the preparation of carbonate of soda; and the dark residual liquor remaining after that salt has crystallized, contains a considerable quantity of iodine, combined with sodium or potassium. By adding a sufficient quantity of sulphuric acid, hydriodic acid is first generated, and then decomposed. The iodine sublimes when the solution is boiled, and may be collected in cool glass receivers. A more convenient process is to employ a moderate excess of sulphuric acid, and then add to the mixture some peroxide of manganese, which acts on hydriodic in the same way as on hydrochloric acid (Phil. Mag. L. Ure). Another method, proposed by Soubeiran, is by adding to the ley from kelp a solution made with the sulphates of protoxides of copper and iron in the ratio of one of the former to $2\frac{1}{4}$ of the latter, as long as a white precipitate appears. The diniodide of copper is thus thrown down; and it may be decomposed either by peroxide of manganese alone, or by manganese and sulphuric acid. By means of the former, the iodine passes over quite dry; but a strong heat is requisite.

---

* The original papers on this subject are in the Annales de Chimie, vols. lxxxviii. xc. and xci.; and in the Philos. Trans. for 1814 and 1815.

Prop.—Iodine, at common temperatures, is a soft friable opaque solid of a bluish-black colour, and metallic lustre. It occurs usually in crystalline scales, having the appearance of micaceous iron ore; but it sometimes crystallizes in large rhomboidal plates, the primitive form of which is a rhombic octohedron. The crystals are best prepared by exposing to the air a solution of iodine in hydriodic acid. Its sp. gr. according to Gay-Lussac, is 4·948; but Thomson found it only 3·0844. At 225° it is fused, and enters into ebullition at 347°; but when moisture is present, it is sublimed rapidly even below the degree of boiling water, and suffers a gradual dissipation at low temperatures. Its vapour is of an exceedingly rich violet colour, a character to which it owes the name of *Iodine.* (From 'Ιώδης, violet-coloured.) This vapour is remarkably dense, its sp. gr. by calculation, page 173, being 8·7011, or 8·716 as directly observed by Dumas. Hence 100 cubic inches, at the standard temperature and pressure, must weigh 269·84 grains.

It is a non-conductor of electricity, and, like oxygen and chlorine, is a — electric. It has a very acrid taste, and its odour is almost exactly similar to that of chlorine, when much diluted with air. It acts energetically on the animal system as an irritant poison, but is employed medicinally in very small doses with advantage.

It is very sparingly soluble in water, requiring about 7000 times its weight of that liquid for solution. It communicates, however, even in this minute quantity, a brown tint to the menstruum. Alcohol and ether dissolve it freely, and the solution has a deep reddish-brown colour.

Iodine possesses an extensive range of affinity. It destroys vegetable colours, though in a much less degree than chlorine. It manifests little disposition to combine with metallic oxides; but it has a strong attraction for the pure metals, and for most of the simple non-metallic substances, producing compounds which are termed *Iodides* or *Iodurets.* It is not inflammable; but under favourable circumstances may, like chlorine, be made to unite with oxygen. A solution of the pure alkalies acts upon it and gives rise to decomposition of water; whether an hypo-iodite and iodide are first produced, as in the case of chlorine, has not yet been determined, but on the application of heat an iodate and iodide are formed.

Pure iodine is not influenced chemically by the imponderables.

Exposure to the direct solar rays, or to strong shocks of electricity, does not change its nature. It may be passed through red-hot tubes, or over intensely ignited charcoal, without any appearance of decomposition; nor is it affected by the agency of galvanism. Chemists, indeed, are unable to resolve it into more simple parts, and consequently it is regarded as an elementary principle.

The violet hue of the vapour of iodine is for many purposes a sufficiently sure indication of its presence. A far more delicate test, however, was discovered by Colin and Gaultier de Claubry. They found that iodine has the property of uniting with starch, and of forming with it a compound insoluble in cold water, which is recognised with certainty by its deep blue colour. This test, according to Stromeyer, is so delicate, that a liquid containing 1 — 450,000th of its weight of iodine receives a blue tinge from a solution of starch. Two precautions should be observed to insure success. In the first place, the iodine must be in a free state; for it is the iodine itself only, and not its compounds, which unites with starch. Secondly, the solution should be quite cold at the time of adding the starch; for hot water dissolves the blue compound, and forms a colourless solution.

Berzelius determined the equivalent of iodine by exposing fused iodide of silver to a current of chlorine gas, whereby the iodine was expelled and chloride of silver generated. Through the known composition of chloride of silver he inferred that of the iodide, and thence found the eq. of iodine. It is 126·3; eq. vol. = 100; symb. I.

The composition of the compounds of iodine described in this section is as follows:—

	Iodine.				Equiv.	Formulæ.
Hydriodic Acid	126·3	1 eq.+	1	1 eq. hydrogen	=127·3.	$H+I$ or HI.
Oxide of Iodine	Composition unknown.					
Iodous Acid						
Iodic Acid	126·3	1 eq.+	40	5 eq. oxygen	=166·3.	IO_5.
Periodic Acid	126·3	1 eq.+	56	7 eq. do.	=182·3.	IO_7.
Protochloride of Iodine	126·3	1 eq.+	35·42	1 eq. chlorine	=161·72.	ICl.
Terchloride do.	126·3	1 eq.+	106·26	3 eq. do.	=232·56.	ICl_3.
Perchloride do.	Composition doubtful.					
Protiodide of Phos.	126·3	1 eq.+	15·7	1 eq. phosphs.	=142·0.	PI.
Sesquiodide do.	378·9	3 eq.+	31·4	2 eq. do.	=410·3.	P_2I_3.
Periodide do.	631·5	5 eq.+	31·4	2 eq. do.	=662·9.	P_2I_5.
Iodide of Sulphur	Composition unknown.					
Iodide of Carbon	Composition unknown.					
Periodide of Carbon	Composition unknown.					
Teriodide of Nitrogen	378·9	3 eq. +	14·15	1 eq. nitrogen	=393·05	NI_3.

Hydriodic Acid.—Prep.—This compound is formed by the direct union of its elements, when a mixture of hydrogen gas and iodine vapour are transmitted through a porcelain tube at a red heat. A more convenient process, and by which it is obtained in a pure state, is by the action of water on the periodide of phosphorus. Any convenient quantity of the iodide is put into a small glass retort, together with a little water, and a gentle heat is applied. Mutual decomposition ensues; the oxygen of the water unites with phosphorus, and its hydrogen with iodine, giving rise to the formation of phosphoric and hydriodic acids, the latter of which passes over in the form of a colourless gas. The preparation of the iodide requires care; since phosphorus and iodine act so energetically on each other by mere contact, that the phosphorus is generally inflamed, and a great part of the iodine expelled in the form of vapour. This inconvenience is avoided by putting the phosphorus into a tube sealed at one end, about twelve inches long, displacing the air by a current of dry carbonic acid gas, then gradually adding the iodine, and promoting the action towards the close by a gentle heat. The materials should be well dried with bibulous paper, and the iodide preserved in a well-stopped dry vessel; for even atmospheric humidity gives rise to copious white fumes of hydriodic acid. The proportions usually employed are one part of phosphorus to about twelve of iodine. Another process has been recommended by F. d'Arcet, which consists in evaporating hypophosphorous acid until it begins to yield phosphuretted hydrogen, mixing it with an equal weight of iodine, and applying a gentle heat. Hydriodic acid gas of great purity is then rapidly disengaged; its production depending, as in the former process, on the decomposition of water.

Prop.—Hydriodic acid gas has a very sour taste, reddens vegetable blue colours without destroying them, produces dense white fumes when mixed with atmospheric air, and has an odour similar to that of hydrochloric acid gas. The salts which it forms with alkalies are called *hydriodates*. Like hydrochloric acid gas, it cannot be collected over water; for that liquid dissolves it in large quantity.

It is decomposed by several substances which have a strong affinity for either of its elements. Thus oxygen gas, when heated with it, unites with its hydrogen, and liberates the iodine. Chlorine effects the decomposition instantly; hydrochloric acid gas is produced, and the iodine appears in the form of vapour. With strong nitrous acid it takes fire, and the vapour of iodine is set free. It is also decomposed by mercury. The decomposition begins as soon as hydriodic acid gas comes in contact with mercury, and proceeds steadily, and even quickly if the gas is agitated, till nothing but hydrogen remains. Gay-Lussac ascertained by this method that 100 measures of hydriodic acid gas contain precisely half their volume of hydrogen. Assuming it to consist of equal volumes of hydrogen gas and iodine vapour united without any condensation, then, since

	Grains.
50 cubic inches of the vapour of iodine weigh . .	134·92
50 do. hydrogen gas . . .	1·0684
100 cubic inches of hydriodic acid gas should weigh .	135·9884.

These numbers are obviously in the ratio of 1 to 126·3, the eq. of iodine and hydrogen. On the same principles the density of the gas should be 4·3850, which is probably more correct than 4·443, a number found experimentally by Gay-Lussac (An. de Ch. xci. 16). From these coincidences there is no doubt that 100 measures of hydriodic acid gas contain 50 measures of hydrogen gas and 50 of the vapour of iodine.

When the gas is conducted into water till that liquid is fully charged with it, a colourless acid solution is obtained, which emits white fumes on exposure to the air, and has a sp. gr. of 1·7. It may be prepared also by transmitting a current of hydrosulphuric acid gas through water in which iodine in fine powder is suspended; or by adding sulphuric acid in atomic proportion to a solution of iodide of barium (Glover). The iodine, from having a greater affinity than sulphur for hydrogen, decomposes the hydrosulphuric acid; and hence sulphur is set free, and hydriodic acid produced. As soon as the iodine has disappeared and become colourless, it is heated for a short time to expel the excess of hydrosulphuric acid, and subsequently filtered to separate free sulphur.

The solution is readily decomposed. On exposure during a few hours to the atmosphere, the oxygen of the air forms water with the hydrogen of the acid, and sets iodine free. The solution is found to have acquired a yellow tint from the presence of uncombined iodine, and a blue colour is occasioned by the addition of starch. Nitric and sulphuric acid likewise decompose it by yielding oxygen, the former being at the same time converted into nitrous, and the latter into sulphurous acid. Chlorine unites directly with the hydrogen of the hydriodic acid, and hydrochloric acid is formed.

The separation of iodine in all these cases may be proved in the way just mentioned. These circumstances afford a sure test of the presence of hydriodic acid, whether free or in combination with alkalies. All that is necessary, is to mix a cold solution of starch with the liquid, previously concentrated by evaporation if necessary, and then add a few drops of strong sulphuric acid. A blue colour will make its appearance if hydriodic acid is present.

Its eq. is 127·3; eq. vol. = 200; symb. $H+I$, or HI.

Oxide of Iodine and Iodous Acid.—On mixing the vapour of iodine and oxygen gas considerably heated, the violet tint of the former disappears, and a yellow matter of the consistence of solid oil is generated, which Sementini regards as oxide of iodine; and if the supply of oxygen be kept up after its formation, it is converted into a yellow liquid, which he supposes to be iodous acid. From the mode in which the process is described, there can scarcely be a doubt that some compound of iodine and oxygen is thus formed; but its composition and properties have not been satisfactorily made out. (Quarterly Journ. of Science, N.S. i. 478.) On dissolving iodine in a rather dilute solution of soda, until the solution begin to acquire a red tint, permanent crystals are obtained by spontaneous evaporation, in six-sided prisms, which dissolve in cold water without change, but by the action of water moderately heated, or by alcohol, are converted into iodate of soda and iodide of sodium. On the addition of an acid, iodine and iodic acid were set at liberty. From these facts Mitscherlich infers the crystals to be iodite of soda. (An. de Ch. et Ph. xxx. 84.) They are more probably the hypo-iodite.

Iodic Acid. — *Hist. and Prep.* — This acid was discovered at about the same time by Gay-Lussac and Davy; but the latter first succeeded in obtaining it in a state of perfect purity. When iodine is brought into contact with the euchlorine of Davy, immediate action ensues; the chlorine unites with one portion of iodine, and the oxygen with another, forming two compounds, a volatile orange-coloured matter, chloride of iodine, and a white solid substance, which is *iodic acid.* On applying heat, the former passes off in vapour, and the latter remains (Phil. Trans. for 1815). Serullas has obtained it, in the form of hexagonal laminæ, by evaporating in a warm place its solution either in water, or in sulphuric or nitric acids. The method which he found most convenient is by forming a solution of iodate of soda in a considerable excess of sulphuric acid, keeping it at a boiling temperature for twelve or fifteen minutes, and then setting it aside to crystallize (Ann. de Ch. et Ph. xliii. 216). Iodic acid may also be formed by dissolving perchloride of iodine in water, and gradually adding a large quantity of strong sulphuric acid, a rise of temperature being at the same time prevented by the application of cold. Iodic acid will then be precipitated. The action of strong alcohol on moist perchloride produces the same result: water and the perchloride decomposed, and hydrochloric and iodic acids formed. The latter is left undissolved by the alcohol. Another process, suggested by Mr. Connell of Edinburgh, is by boiling iodine in nitric acid. For this purpose a pure acid of density 1·5 should be introduced with about a fifth of its weight of iodine into a tube sealed at one end, about an inch wide and 15 inches long, and these materials be kept at a boiling temperature for at least twelve hours. As the iodine rises and condenses on the sides of the tube, it should be restored to the liquid, either by agitation or by help of a glass rod. As soon as the iodine disappears, the nitric acid is dissipated by cautious evaporation. It is also obtained, as remarked by Balard, by the oxidizing effect of hypochlorous acid on iodine; the latter unites with the oxygen of the acid, and the chlorine escapes in the gaseous state.

Prop.—This compound, which was termed *oxiodine* by Davy, is *anhydrous iodic acid.* It is a white semitransparent solid, which has a strong astringent sour taste, but no odour. Its sp. gr. is considerable, as it sinks rapidly in sulphuric acid. When heated to the temperature of about 500° F. it is fused, and at the same time resolved into oxygen and iodine. In a dry air it is unchanged; but in a moist atmosphere it absorbs humidity, forming the hydrated acid, and eventually deliquesces. In water it is very soluble, and the solution has a distinct acid reaction: the bleaching power ascribed to it by Davy is said by Hiley not to be a property of pure iodic acid. (Lancet for July 1833.) On evaporating the solution, a thick mass of the consistence of paste is left, which is hydrous iodic acid; and which, by the cautious application of heat, may be rendered anhydrous. It acts powerfully on inflammable substances. With charcoal, sulphur, sugar, and similar combustibles, it forms mixtures which detonate when heated. It enters into combination with metallic oxides, and the resulting salts are called *iodates.* These compounds, like the chlorates, yield pure oxygen by heat, and deflagrate when thrown on burning charcoal.

Iodic acid forms with the pure alkalies salts which are soluble in water; but with lime, baryta, strontia, and the oxides of lead and silver, it yields compounds of very sparing solubility. It is readily detected by the facility with which it is deoxidized, an effect readily produced by the sulphurous, phosphorous, hydriodic, and hydrosulphuric acids. Iodine in each case is set at liberty, and may be detected as usual by starch. Hydrochloric and iodic acids decompose each other, water and chloride of iodine being generated.

Davy ascertained the composition of iodic acid by determining the quantity of oxygen which the acid loses when decomposed by heat; Gay-Lussac arrived at the same result by heating iodate of potassa, when pure oxygen was given off and iodide of potassium remained. Its eq. is 166·3; symb. $I + 5O$, $\overset{\cdot\because\cdot}{I}$, or IO_5.

Periodic Acid.—Hist. and Prep.—This compound has been lately discovered by Ammermüller and Magnus. (Pogg. Annalen, xxviii. 514.) When pure soda is mixed with a solution of iodate of soda, and chlorine gas is transmitted into it to saturation, a sparingly soluble white pulverulent salt is generated, which subsides after heating, and if necessary, concentrating the solution. This salt is a periodate of soda, the production of which appears to depend on the formation of chloride of sodium, and the union of the oxygen of the soda with the iodine of the iodic acid. For each equivalent of periodic acid, 2 eqs. of chloride of sodium should be generated; since the materials IO_5, $2NaO$, $2Cl$, just suffice for yielding IO_7, and $2NaCl$. On dissolving the periodate of soda in dilute nitric acid, and adding nitrate of oxide of silver, the periodate of this oxide of a greenish-yellow colour subsides, which should be washed with water acidulated with nitric acid. This yellow salt is soluble in hot dilute nitric acid, and separates again on cooling in small shining straw-yellow crystals, which by digestion with warm water acquire, without dissolving, a reddish-brown almost black colour. If the nitric acid solution of the yellow salt is so far concentrated by evaporation that it crystallizes while still warm, orange-coloured crystals subside. These three salts are readily analyzed by exposure to a red heat in a glass tube, when iodine and metallic silver remain in the tube, and oxygen gas along with water, when water is present, is expelled. Their composition is as follows:—

	Oxide of Silver.		Periodic Acid.		Water.		Formulæ.
Yellow Salt	232	2 eq.	182·3	1 eq.	27	3 eq.	$IO_7, 2AgO, 3aq.$
Red Salt	232	2 eq.	182·3	1 eq.	18	2 eq.	$IO_7, 2AgO, 2aq.$
Orange Salt	116	1 eq.	182·3	1 eq.	0		$IO_7, AgO.$

The two former are therefore hydrated subperiodates of oxide of silver, and the latter a neutral periodate. This neutral salt has the peculiarity, that by pure cold water it is converted into the yellow subsalt, while the water takes up exactly half of its acid without a trace of silver. By this means a pure solution of periodic acid may be obtained.

Prop.—Periodic acid is analogous in composition to perchloric acid, and has decided acid properties. Its solution may be boiled without decomposition, and on evaporation the acid yields crystals, which do not change by exposure to the air. By hydrochloric acid it is reduced to iodic acid with disengagement of chlorine, and the same change will of course be produced by substances which decompose iodic acid. When the heat is increased beyond 212°, (the precise point is not stated,) periodic acid loses oxygen, and iodic acid remains. Thus is periodic more easy of decomposition than iodic acid. Its eq. is 182·3; symb. $I + 7O$, $\overset{\cdot\cdot\cdot\cdot\cdot\cdot\cdot}{I}$, or IO_7.

Chlorides of Iodine.—Chlorine is absorbed at common temperatures by dry iodine with evolution of heat, and a solid compound of iodine and chlorine results, which was discovered both by Davy and Gay-Lussac. The colour of the product is orange-yellow when the iodine is fully saturated with chlorine, but is of a reddish-orange if iodine is in excess. It is converted by heat into an orange coloured liquid, which yields a vapour of the same tint on increase of temperature. It deliquesces in the open air, and dissolves freely in water. Its solution is colourless, very sour to the taste, and reddens vegetable blue colours, but afterwards destroys them. From its acid properties Davy gave it the name of *chloriodic acid.* Gay-Lussac, on the contrary, calls it *chloride of iodine*, conceiving that the acidity of its solution arises from the presence of hydrochloric and iodic acids, which he supposes to be generated by decomposition of water. From the observations of Serullas and Dumas it appears that there exist two compounds of chlorine and iodine, by the different action of which on water the discordant opinions of Davy and Gay-Lussac may be explained.

This subject has lately been examined by Soubeiran. He has distinguished a compound of three eq. of chlorine and one eq. of iodine, but doubts the existence of the perchloride of iodine of Davy and Gay-Lussac (Journal de Pharmacie, Feb. 1837). This compound and a protochloride appears, however, to have been previously described by Kane (Phil. Mag. x. 430). The protochloride was obtained by passing a current of chlorine gas into water, in which iodine was diffused. A deep reddish yellow solution is formed, which gives off fumes irritating to the eyes and nose, has a peculiar smell of both its constituents, and first reddens and then bleaches litmus paper. The terchloride was obtained by repeatedly distilling the protochloride; it may also be procured by adding to the protochloride a strong solution of corrosive sublimate, which throws down iodine. The perchloride is supposed to contain 5 eq. of chlorine and 1 eq. of iodine, from giving rise, when decomposed by water, to hydrochloric and iodic acids.

Teriodide of Nitrogen. — From the weak affinity that exists between iodine and nitrogen, these substances cannot be made to unite directly. But when iodine is put into a solution of ammonia, the alkali is decomposed; its elements unite with different portions of iodide, and thus cause the formation of hydriodic acid and iodide of nitrogen. The latter subsides in the form of a dark powder, which is characterised, like quadrochloride of nitrogen, by its explosive property. It detonates violently as soon as it is dried; and slight pressure, while moist, produces a similar effect. Heat and light are emitted during the explosion, and iodine and nitrogen are set free. According to the experiments of M. Colin, iodide of nitrogen consists of one eq. of nitrogen and three of iodine.

It is conveniently made, according to Serullas, by saturating alcohol of 0·852 with iodine, adding a large quantity of pure ammonia, and agitating the mixture. On diluting with water, teriodide of nitrogen subsides, which should be washed by repeated affusion of water and decantation. As thus prepared it is very finely divided, and may be pressed under water without detonating; but if, subsequently to its formation, it is put in contact with pure ammonia, it will afterwards detonate with the same facility as that prepared in the usual manner. Water and teriodide of nitrogen mutually decompose each other, giving rise to the formation of hydriodic and iodic acids and ammonia. The change takes place slowly in cold water; but it is completed in a few minutes, and with scarcely any disengagement of nitrogen, when gentle heat is applied. When a little nitric or sulphuric acid is used, ammonia and iodic acid are alone produced. (An. de Ch. et Ph. xlii. 201.)

Its eq. 393·05; symb. $N + 3I$, or NI_3.

Iodides of Phosphorus.—Iodine and phosphorus combine readily in the cold, evolving so much heat as to kindle the phosphorus, if the experiment is made in the open air; but in close vessels no light appears. One of these compounds, apparently a protiodide, is formed of one part of phosphorus and 7 or 8 parts of iodine. It has an orange colour, fuses at 212°, sublimes unchanged by heat, and is decomposed by water, with the elements of which it gives rise to hydriodic and phosphorous acids, while phosphorus is set free. Its eq. is 142·0; symb. $P + I$, or PI.

The sesquiodide is formed by the action of 1 part of phosphorus and 12 of iodine. It appears as a dark grey crystalline mass, fusible at 84°, and yields with water hydriodic and phosphorous acids, from which circumstance its elements are supposed to be in the ratio of 2 eq. of phosphorus to 3 eq. of iodine.

Its eq. is 410·3; symb. $2P + 3I$, or P_2I_3.

The periodide is prepared with 1 part of phosphorus and 20 of iodine, and is a black compound, fusible at 114°. As by the action of water it yields hydriodic and phosphoric acids only, it is inferred to contain phosphorus and iodine in the ratio of 2 eq. to 5 eq. Thus

1 eq. Periodide Phos. & 5 eq. water	yield	1 eq. Phos. Acid. & 5 eq. Hydriodic Acid.
P_2I_5+5HO		P_2O_5+5HI.

Its eq. is 662·9; symb. $2P + 5I$, or P_2I_5.

Iodide of Sulphur.—This compound is formed by heating gently 4 parts of iodine with 1 of sulphur. The product has a dark colour and radiated appearance, like antimony. Its elements are easily disunited by heat.

SECTION XIV.

BROMINE.

Bromine was discovered in 1826 by Balard of Montpellier. The name originally applied to it was *muride*, but the term *brome* or *bromine*, from *βρωμος graveolentia*, signifying a strong or rank odour, has since been substituted (An. of Phil. xviii. 381).

Bromine in its chemical relations bears a close analogy to chlorine and iodine, and has hitherto been always found in nature associated with the former, and sometimes also with the latter. It exists in sea-water in the form of bromide of sodium or magnesium. Its relative quantity, however, is very minute; and even the uncrystallizable residue called *bittern*, left after chloride of sodium has been separated from sea-water by crystallization, contains it in small proportion. It may apparently be regarded as an essential ingredient of the saline matter of the ocean; for it has been detected in the waters of the Mediterranean, Baltic, North Sea, and Frith of Forth. It has also been found in the waters of the Dead Sea, and in a variety of salt springs in Germany. Daubeny has detected it in several mineral springs in England, and states that it is rarely wanting in those springs which contain much common salt, except that of Droitwich in Worcestershire. Balard found that it exists in marine plants growing on the shores of the Mediterranean, and has procured it in appreciable quantity from the ashes of sea-weeds that furnish iodine. He has likewise detected its presence in the ashes of some animals, especially in those of the *Janthina violacea*, one of the testaceous mollusca.

Prep.—Bromine is usually extracted from bittern, and its mode of preparation is founded on the property which chlorine possesses of decomposing hydrobromic acid, uniting with its hydrogen, and setting bromine at liberty. Accordingly, on adding chlorine to bittern, the free bromine immediately communicates an orange-yellow tint to the liquid; and on heating the solution to its boiling point, the red vapours of bromine are expelled, and may be condensed by being conducted into a tube surrounded with ice. It was this change of colour produced by chlorine that led to the discovery of bromine. The method recommended by Balard for procuring this substance, as well as for detecting the presence of hydrobromic acid, is to transmit a current of chlorine gas through bittern, and then to agitate a portion of sulphuric ether with the liquid. The ether dissolves the whole of the bromine, from which it receives a beautiful hyacinth-red tint, and on standing it rises to the surface. When the ethereal solution is agitated with caustic potassa, its colour entirely disappears, owing to the formation of bromide of potassium and bromate of potassa, the former of which is obtained in cubic crystals by evaporation. The bromine may then be set free by means of chlorine, or still better by sulphuric acid and the peroxide of manganese. The process should be conducted in a retort, the beak dipping into cold water, which collects the bromine driven over by heat. Balard has subsequently improved the process so much, that it is now produced in considerable quantity, and sold in Paris as an article of commerce.

Prop.—At common temperatures bromine is a liquid, the colour of which is blackish-red when viewed in mass and by reflected light, but appears hyacinth-red when a thin stratum is interposed between the light and the observer. Its odour, which somewhat resembles that of chlorine, is very disagreeable, and its taste powerful. Its sp. gr. is about 3. By a temperature between zero and −4° it is congealed, and in that state is brittle. Its volatility is considerable; for at common temperatures it emits red-coloured vapours, which are very similar in appearance to those of nitrous acid; and at 116·5° it enters into ebullition. The sp. gr. of its vapour was found by Mitscherlich to be 5·54, and the number calculated (p. 173) from its equivalent is 5·3930: 100 cubic inches at 60° and 30 inches B. should weigh 167·25 grains. It is a non-conductor of electricity, and undergoes no chemical change whatever from the agency of the imponderables. It may be transmitted through a red-hot glass tube, and be exposed to the agency of galvanism, without evincing the least trace of decomposition. Like oxygen, chlorine, and iodine, it is a negative electric. It is soluble in water, alcohol, and ether, the latter being its best solvent. It does not redden litmus paper, but bleaches it rapidly like chlorine; and it likewise discharges the blue colour from a solution of indigo. Its vapour extinguishes a lighted taper; but before going out, it burns for a few seconds with a flame which is green at its base and red at its upper part. Some inflammable substances take fire by contact with bromine, in the same manner as when introduced into an atmosphere of chlorine. It acts with energy on organic matters, such as wood or cork, and corrodes the animal texture; but if applied to the skin for a short time only, it communicates a yellow stain, which is less intense than that produced by iodine, and soon disappears. To animal life it is highly destructive, one drop of it placed on the beak of a bird having proved fatal.

From the close resemblance observable between chlorine and bromine, Balard was of course led to examine its relations with hydrogen, and found that these substances may readily be made to unite; the product of the combination being a gas very similar to hydrochloric and hydriodic acid gases, whence it has received the name of *hydrobromic* acid gas. In its action on metals, also, bromine presents the closest similarity to that which chlorine exerts on the same substances. Antimony and tin take fire by contact with bromine; and its union with potassium is attended with such intense heat as to cause a vivid flash of light, and often to burst the vessel in which the experiment is performed. Its affinity for metallic oxides is feeble. By the action of alkalies it is resolved into hydrobromic and bromic acids, suffering the same kind of change as chlorine or iodine when similarly treated.

According to all the experiments hitherto made, bromine appears to be an element. It is so very similar in most aspects to chlorine and iodine, and in the order of its chemical relations is so constantly intermediate between them, that Balard at first supposed it to be some unknown compound of these substances. There seems, however, to be no good ground for the supposition; but, on the contrary, an experiment performed by De la Rive affords a very strong argument against it. He finds that when a compound of bromine and iodine is mixed with starch, and exposed to the influence of galvanism, bromine appears at the + and iodine at the — wire, where the starch acquires a blue tint. On making the experiment with bromine containing a little bromide of iodine, the same appearance ensues; but if iodine is not previously added, the starch does not receive a tint of blue.

Bromine is in most cases easily detected by means of chlorine; for this substance displaces bromine from its combination with hydrogen, metals, and most other bodies. The appearance of its vapour or the colour of its solution in ether will then render its presence obvious. Like chlorine, it forms a crystalline hydrate when exposed to 32° F. in contact with water. The crystals are octohedral, of a beautiful red tint, and suffer decomposition at 54°. (Löwig.)

Berzelius determined the equivalent of bromine in the same way as that of iodine, namely, by heating a known weight of bromide of silver in a current of chlorine gas, so as to displace the bromine and obtain chloride of silver.

Its eq. is 78·4; eq. vol. = 100; symb. Br.

The compounds of bromine described in this section are as follows:—

	Bromine.		Equiv.		Formulæ.
Hydrobromic Acid .	78·4	1 eq.+Hydrogen	1	1 eq.= 79·4.	HBr.
Bromic Acid . .	78·4	1 eq.+Oxygen	40	5 eq.=118·4.	BrO_5.
Chloride of Bromine	Composition uncertain.				
Bromides of Iodine .	Composition uncertain.				
Bromide of Sulphur	Composition uncertain.				
Protobromide of Phosp.	78·4	1 eq +phosph.	15·7	1 eq.= 94·1.	PBr.
Perbromide of Phosp.	392	5 eq.+ do.	31·4	2 eq.=423·4.	P_2Br_5.
Bromide of Carbon	Composition uncertain.				
Terbromide of Silicon	235·2	3 eq.+Silicon	22·5	1 eq =257·7.	$SiBr_3$.

Hydrobromic Acid.—*Prep.*—No chemical action takes place between the vapour of bromine and hydrogen gas at common temperatures, not even by the agency of the direct solar rays; but on introducing a lighted candle, or a piece of red-hot iron, into the mixture, combination ensues in the vicinity of the heated body, though without extending to the whole mixture, and without explosion. The combination is readily effected by the action of bromine on some of the gaseous compounds of hydrogen. Thus, on mixing the vapour of bromine with hydriodic acid, hydrosulphuric acid, or phosphuretted hydrogen gases, decomposition ensues, and hydrobromic acid gas is generated. It may be conveniently made for experimental purposes by a process similar to that for forming hydriodic acid. A mixture of bromine and phosphorus, slightly moistened, yields, by the aid of gentle heat, a large quantity of pure hydrobromic acid gas, which should be collected either in dry glass bottles, or over mercury.

Prop.—It is a colourless gas, has an acid taste, and pungent odour. It irritates the glottis powerfully, so as to excite cough, and when mixed with moist air, yields white vapours, which are denser than those occasioned under the same circumstances by hydrochloric acid gas. It undergoes no decomposition when transmitted through a red-hot tube, either alone, or mixed with oxygen. It is not affected by iodine; but chlorine decomposes it instantly, with production of hydrochloric acid gas, and deposition of bromine. It may be preserved without change over mercury; but potassium and tin decompose it with facility, the former at common temperatures, and the latter by the aid of heat. It is very soluble in water. The aqueous solution may be made by treating bromine with hydrosulphuric acid dissolved in water, or still better, by transmitting a current of hydrobromic acid gas into pure water. The liquid becomes hot during the condensation, acquires great density, increases in volume, and emits white fumes when exposed to the air. This acid solution is colourless when pure, but possesses the property of dissolving a large quantity of bromine, and then receives the tint of that substance.

Chlorine decomposes the solution of hydrobromic acid in an instant. Nitric acid likewise acts upon it, though less suddenly, occasioning the disengagement of bromine, and probably the formation of water and nitrous acid. Nitro-hydrobromic acid is analogous to *aqua regia*, and possesses the property of dissolving gold. The elements of sulphuric and hydrobromic acids react on each other in a slight degree; and hence, on decomposing bromide of potassium by sulphuric acid, the hydrobromic is generally mixed with a little sulphurous acid gas.

The composition of hydrobromic acid gas is easily inferred from the two following facts. 1. On decomposing hydrobromic acid gas by potassium, a quantity of hydrogen remains, precisely equal to half the volume of the gas employed; and, 2, when hydriodic acid gas is decomposed by bromine, the resulting hydrobromic acid occupies the very same space as the gas which is decomposed. Hence hydrobromic is analogous to hydriodic and hydrochloric acid gases, in containing equal measures of bromine vapour and hydrogen gas united without any change of volume; and since

			Grains.
50	cubic inches of	Bromine vapour weigh . . .	83·64
50	do.	Hydrogen gas	1·0684
100	do.	Hydrobromic acid must weigh . .	84·7084

These numbers are in the ratio of 1 to 78·4, which is the composition of the gas by weight. Its sp. gr. is 2·731.

Since bromine decomposes hydriodic, and chlorine hydrobromic acid, bromine, in relation to hydrogen, is intermediate between chlorine and iodine; for it has a stronger affinity for hydrogen than iodine, and a weaker than chlorine. The affinity of bromine and oxygen for hydrogen appears nearly similar; for while oxygen cannot detach hydrogen from bromine, bromine does not decompose watery vapour.

The salts of hydrobromic acid are termed *hydrobromates.* Like the free acid, they are decomposed, and the presence of bromine is detected, by means of chlorine. On mixing a soluble bromide with the nitrates of the protoxides of lead, silver, and mercury, white precipitates are obtained, which are very similar in appearance to the chlorides of those metals, but which are metallic bromides. On the addition of chlorine, the vapour of bromine is evolved.

Its eq. is 79·4; eq. vol. $=200$; symb. $H+Br$, or $H\,Br$.

Bromic Acid.—Prep.—The only compound yet known of bromine and oxygen is that formed by the action of bromine on potassa, when a change exactly similar to that produced by chlorine (page 285) ensues, whereby bromide of potassium and bromate of potassa are generated; and the latter, being much less soluble than the former, is readily separated by evaporation. The bromate of the other alkalies and alkaline earths may be prepared in a similar manner.

The acid may be procured in a separate state by decomposing a dilute solution of bromate of baryta with sulphuric acid, so as to precipitate the whole of the baryta. The resulting solution of bromic acid may be concentrated by slow evaporation until it acquire the consistence of syrup; but on raising the temperature, in order to expel all the water, one part of the acid is volatilized, and the other resolved into oxygen and bromine. A similar result took place when the evaporation was conducted *in vacuo* with sulphuric acid; and accordingly all attempts to procure anhydrous bromic acid have hitherto failed.

Prop.—Bromic acid has scarcely any odour, but its taste is very acid, though not at all corrosive. It reddens litmus paper powerfully at first, and soon after destroys its colour. It is not affected by nitric or sulphuric acids except when the latter is highly concentrated, in which case bromine is set free, and effervescence, probably owing to the escape of oxygen gas, ensues. From the analysis of bromate of potassa, bromic acid is obviously similar in constitution to iodic, chloric, and nitric acids; that is, it consists of one equivalent of bromine united with five of oxygen. Its salts are analogous to the chlorates and iodates. Thus bromate of potassa is converted by heat into bromide of potassium, with disengagement of pure oxygen gas, deflagrates like nitre when thrown on burning charcoal, and forms with sulphur a mixture which detonates by percussion. The acid of the bromates is decomposed by deoxidizing agents, such as sulphurous and hydrosulphuric acids, in the same manner as the acid of the iodates. The bromates likewise suffer decomposition from the action of hydrobromic and hydrochloric acids.

Bromate of potassa is said not to precipitate the salts of lead, but to occasion a white precipitate with nitrate of silver, and a yellowish-white with protonitrate of mercury; characters which, if true, serve as a good test to distinguish bromate from iodate and chlorate of potassa.

Its eq. is 118·4; symb. $\mathrm{Br}+5\mathrm{O}$, $\overset{:\cdot:}{\mathrm{Br}}$, or BrO_5.

Chloride of Bromine.—This compound may be formed at common temperatures by transmitting a current of chlorine through bromine, and condensing the disengaged vapours by means of a freezing mixture. The resulting chloride is a volatile fluid of a reddish-yellow colour, much less intense than that of bromine; its odour is penetrating, and causes a discharge of tears from the eyes; and its taste very disagreeable. Its vapour is a deep yellow, like chlorous acid, and it enables metals to burn as in an atmosphere of chlorine, doubtless giving rise to the formation of metallic chlorides and bromides.

Chloride of bromine is soluble in water without decomposition;

for the solution possesses the colour, odour, and bleaching properties of the compound, and discharges the colour of litmus paper without previously reddening it. By the action of the alkalies it is decomposed, being converted, by means of the elements of water, into hydrochloric and bromic acids.

Bromide of Iodine.—These substances act readily on each other, and appear capable of uniting in two proportions. The protobromide is a solid, convertible by heat into a reddish-brown vapour, which, in cooling, condenses into crystals of the same colour, and of a form resembling that of fern leaves. An additional quantity of bromine converts these crystals into a fluid, which in appearance is like a strong solution of iodine in hydriodic acid. This compound dissolves without decomposition in water, but with the alkalies yields hydrobromic and iodic acids. The existence of two bromides of iodine can scarcely be regarded as satisfactorily established.

Bromide of Sulphur.—On pouring bromine on sublimed sulphur, combination ensues, and a fluid of an oily appearance and reddish tint is generated. In odour it somewhat resembles chloride of sulphur, and like that compound emits white vapours when exposed to the air; but its colour is deeper. It reddens litmus paper faintly when dry, but strongly if water is added. Cold water acts slowly upon bromide of sulphur; but at a boiling temperature the action is so violent that a slight detonation occurs, and three compounds, hydrobromic, hydrosulphuric, and sulphuric acids are formed. The formation of these substances is of course attributable to decomposition of water, and the union of its elements with bromine and sulphur. Bromide of sulphur is likewise decomposed by chlorine, which unites with sulphur, and displaces bromine.

The composition of bromide of sulphur is unknown. It dissolves an excess both of chlorine and sulphur, and its elements separate from each other so readily, that it has hitherto been impracticable to procure a definite compound.

Bromide of Phosphorus.—When bromine and phosphorus are brought into contact in a flask filled with carbonic acid gas, they act suddenly on each other with evolution of heat and light, and two compounds are generated: one, a crystalline solid, which is sublimed and collects in the upper part of the flask; and the other, a fluid, which remains at the bottom. The former contains the most bromine, and the latter is supposed by Balard to consist of single equivalents of its elements.

The protobromide retains its liquid from even at 52° F. It is readily converted into vapour by heat, and on exposure to the air emits penetrating fumes. It reddens litmus paper faintly, an effect which is probably owing to the presence of moisture. With water it acts energetically and with free disengagement of heat, hydrobromic acid gas being evolved when only a few drops of water are employed; but if a large quantity is used, the gas is dissolved, and the acid solution leaves by evaporation a residuum, which burns slightly when dried, and is converted into phosphoric acid.

The perbromide is yellow in its solid state; but with gentle heat it becomes a red-coloured liquid, which by increase of temperature is converted into a vapour of the same tint. On cooling after fusion it yields rhombic crystals; but when its vapour is condensed, the crystals are acicular. It is decomposed by metals, probably with the formation of metallic bromides and phosphurets. It emits dense penetrating fumes on exposure to the air, and with water gives rise to the production of hydrobromic and phosphoric acids. Hence its elements should be in the ratio of 2 eqs. of phosphorus to 5 eqs. of bromine.

Chlorine has a greater affinity for phosphorus than bromine, and decomposes both the bromides with evolution of the vapour of bromine. These compounds are not decomposed by iodine; but, on the contrary, bromine decomposes iodide of phosphorus.

Terbromide of Silicon.—This compound was made by Serullas in precisely the same mode as that described for forming the terchloride. When purified from free bromine by mercury, and redistilled, it is a colourless liquid, which emits dense vapours in an open vessel, being decomposed by the moisture of the air, and is denser than strong sulphuric acid. At 302° it enters into ebullition, and freezes at 10°. Potassium, when gently heated, acts on it with such energy that detonation ensues. By water it is resolved into hydrobromic and silicic acids. (Phil. Mag. and Annals, xi. 295.) Its eq. is 257·7; symb. $Si + 3Br$, or $Si\,Br_3$.

SECTION XV.

FLUORINE.

The substance to which this name is applied, though long known to exist in various compounds, has only recently been obtained in an insulated form, and therefore the properties peculiar to it in that state are but imperfectly known. It was first procured by Baudrimont by passing fluoride of boron over minium heated to redness, and receiving the gas in a dry vessel. As it is mixed with a large quantity of oxygen, his present method is to treat a mixture of fluoride of lime and peroxide of manganese with strong sulphuric acid. This process, however, does not give a pure gas, as hydrofluoric and fluosilicic acid gases are at the same time evolved. The presence of the latter do not prevent the observation of some of the properties of fluorine. It is a gas of a yellowish-brown colour; its odour resembles chlorine and burnt sugar; it bleaches. It does not act on glass, but combines directly with gold (Phil. Mag. x. 149). The latter fact is confirmed by the observations of Messrs. Knox, who have succeeded so far in the preparation of fluorine as to leave no doubt of its existence as a coloured gas (Phil. Mag. x. 107). Its sp. gr. is 1·289. From the nature of its compounds it appears to belong to the class of negative electrics, and, like oxygen and chlorine, to have a powerful affinity for hydrogen and metallic substances. Berzelius determined its eq. by finding that 100 parts of pure fluoride of calcium yield with sulphuric acid 175 parts of sulphate of lime. Its eq. is 18·68; eq. vol. = 100; symb. F.

The compounds of fluorine described in this section are the following:—

	Fluorine.			Equiv.	Formulæ.
Hydrofluoric acid	18·68	1 eq.+Hydrogen	1.	1 eq. = 19·68.	HF.
Fluoboric acid	56·08	3 eq.+Boron	10·9	1 eq. = 66·98.	BF_3.
Fluosilicic acid	56·08	3 eq.+Silicon	22·5	1 eq. = 78·58.	SiF_3.

Hydrofluoric Acid.—Hist. and Prep.—This acid was first procured in its pure state in the year 1810 by Gay-Lussac and Thenard, and described in the second volume of their *Recherches Physico-Chimiques.* It is prepared by acting on the mineral called *fluor-spar*, which is a fluoride of calcium, carefully separated from siliceous earth and reduced to fine powder, with twice its weight of concentrated sulphuric acid. The mixture is made in a leaden retort; and on applying heat, an acid and highly corrosive vapour distils over, which must be collected in a receiver of the same metal surrounded with ice. As the materials swell up considerably during the process, owing to a quantity of vapour forcing its way through a viscid mass, the retort should be capacious. At the close of the operation pure hydrofluoric acid is found in the receiver, and the retort contains dry sulphate of lime. The chemical changes are precisely the same as in the formation of hydrochloric acid gas at page 277, fluorine being substituted for chlorine and calcium for sodium. If the oil of vitriol is of sufficient strength, all its water is decomposed, and the resulting hydrofluoric acid is anhydrous.

Prop.—It is at 32° a colourless fluid, and remains in that state at 59° if preserved in well-stopped bottles; but when exposed to the air, it flies off in dense white fumes, which consist of the acid vapour combined with the moisture of the atmosphere. Its sp. gr. is 1·0609; but its density may be increased to 1·25 by gradual additions of water. Its affinity for this liquid far exceeds that of the strongest sulphuric acid, and the combination is accompanied with a hissing noise, as when red-hot iron is quenched by immersion in water.

Its vapour is much more pungent than chlorine or any of the irritating gases. Of all known substances, it is the most destructive to animal matter. When a drop of the concentrated acid of the size of a pin's head comes in contact with the skin, instantaneous disorganization ensues, and deep ulceration of a malignant character is produced. On this account the greatest care is requisite in its preparation. It acts energetically on glass. The transparency of the glass is instantly destroyed, heat is evolved, and the acid boils, and in a short time entirely disappears. A colourless gas, commonly known by the name of *fluo-silicic acid gas*, is the sole product. This compound is always formed when hydrofluoric acid comes in contact with a siliceous substance. For this reason it cannot be preserved in glass; but must be prepared and kept in metallic vessels. Those of lead, from their cheapness, are often used; but vessels of silver or platinum are preferable. It consequence of its powerful affinity for siliceous matter, hydrofluoric acid may be employed for etching on glass; and when used with this intention, it should be diluted with three or four times its weight of water.

Hydrofluoric acid has all the usual characters of a powerful acid. It has a strong sour taste, reddens litmus paper, and neutralizes alkalies, either forming salts termed *hydrofluates*, or most generally giving rise to metallic fluorides. All these compounds are decomposed by strong sulphuric acid with the aid of heat, and the hydrofluoric acid while escaping may be detected by its action on glass.

On some of the metals it acts violently, especially on the bases of the alkalies. Thus when potassium is brought in contact with the concentrated acid, an explosion attended with heat and light ensues; hydrogen gas is disengaged, and a white compound, fluoride of potassium, is generated. It is a solvent for some elementary principles which resist the action even of nitro-hydrochloric acid. Thus it dissolves silicon, zirconium, and columbium, with evolution of hydrogen gas; and when mixed with nitric acid, it proves a solvent for silicon which has been condensed by heat, and for titanium. Nitro-hydrofluoric acid, however, is incapable of dissolving gold and platinum. Several oxidized bodies, which are not attacked by sulphuric, nitric, or hydrochloric acid, are readily dissolved by hydrofluoric acid. As examples of this fact, several of the weaker acids, such as silica or silicic acid, titanic, columbic, molybdic, and tungstic acids may be enumerated. (Berzelius.)

A different view of the compounds of fluorine was originally taken by Gay-Lussac and Thenard, and is still held by some chemists. They adopted the opinion that hydrofluoric acid is a compound of a certain inflammable principle and oxygen, and applied to it the name of *fluoric acid*, previously introduced by Scheele. Fluor-spar on this view is a fluate of lime, and when this salt is decomposed by oil of vitriol, the fluoric is merely displaced by the sulphuric acid, and the former passes off combined with the water of the latter. What I have described as anhydrous hydrofluoric acid is, according to this hypothesis hydrated fluoric acid; and when acted upon by potassium, this metal is oxidized at the expense of the water, and potassa thus generated unites with fluoric acid, forming, not fluoride of potassium, but fluate of potassa. The equivalent of fluoric acid, as inferred from the analysis of Berzelius, is 10·68; for 39·18 parts or one equivalent of fluor-spar is supposed to contain 28·5 parts of lime (20·5 calcium and 8 oxygen), thus leaving 10·68 as the equivalent of the acid.

The theory, according to which fluor-spar is a compound of fluorine and calcium, originated as a suggestion with M. Ampère of Paris, and was afterwards supported experimentally by Davy. It was found that pure hydrofluoric acid evinces no sign of containing either oxygen or water. Charcoal may be intensely heated in the vapour of the acid without the production of carbonic acid. When hydrofluoric acid was neutralized with dry ammoniacal gas, a white salt resulted, from which no water could be separated; and on treating this salt with potassium, no evidence could be obtained of the presence of oxygen. On exposing the acid to the agency of galvanism, there was a disengagement at the negative pole of a small quantity of gas, which from its combustibility was inferred to be hydrogen; while the platinum wire of the opposite side of the battery was rapidly corroded, and became covered with a chocolate coloured powder. Davy explained these phenomena by supposing that hydrofluoric acid was resolved into its elements; and that fluorine, at the moment of arriving at the positive side of the battery, entered into combination with the platinum wire which was employed as a conductor. Unfortunately, however, he did not succeed in obtaining fluorine in an insulated state. Indeed, from the noxious vapours that arose during the experiment, it was impossible to watch its progress, and examine the different products with that precision which is essential to the success of minute chemical inquiries, and which Davy has so frequently displayed on other occasions.

Though these researches led to no conclusive result, they afforded so strong a presumption in favour of the opinion of Ampère and Davy, that it was adopted by several other chemists. This view has received strong additional support from the experiments of M. Kuhlman. (Quarterly Journal of Science for July 1827, p. 205.) It was found by this chemist that fluor-spar is not in the slightest degree decomposed by the action of anhydrous sulphuric acid, whether at common temperatures or at a red heat. The experiment was made both by transmitting the vapour of anhydrous sulphuric acid over fluor-spar heated to redness in a tube of platinum, and by putting the mineral into the liquid acid. In neither case did decomposition ensue; but when the former experiment was repeated with the difference of employing concentrated hydrous instead of anhydrous sulphuric acid, evolution of hydrofluoric acid was produced. M. Kuhlman also transmitted hydrochloric acid gas over fluor-spar at a red heat, when hydrofluoric acid was disengaged, without any evolution of hydrogen, and chloride of calcium remained. I am aware of no satisfactory explanation of these facts, except by regarding fluor-spar as a compound of fluorine and calcium, and hydrofluoric acid as a compound of fluorine and hydrogen. I shall accordingly adopt this view in the subsequent pages, and never employ the term fluoric acid except when explaining phenomena according to the theory of Gay-Lussac.

Its eq. is 19·68; symb. $H + F$, or HF.

Fluoboric Acid.—Prep.—The chief difficulty in determining the nature of hydrofluoric acid arises from the water of the sulphuric acid which is employed in its preparation. To avoid this source of uncertainty, Gay-Lussac and Thenard made a mixture of vitrified boracic acid and fluor-spar, and exposed it in a leaden retort to heat, under the expectation that as no water was present, anhydrous fluoric acid would be obtained. In this, however, they were disappointed; but a new gas came over, to which they applied the term of *fluoboric acid gas*. A similar train of reasoning led Davy about the same time to the same discovery; though the French chemists had the advantage in priority of publication. Another process given by Dr. Davy, is to mix 1 part of vitrified boracic acid and 2 of fluor-spar with 12 parts of strong sulphuric acid, heating the mixture gently in a glass flask (Phil. Trans. 1812); but the gas thus developed contains a considerable quantity of fluosilicic acid. Fluoboric acid gas may also be formed by heating a strong solution of hydrofluoric and boracic acids in a metallic retort.

In the decomposition of fluor-spar by vitrified boracic acid, the former and part of the latter undergo an interchange of elements. The fluorine uniting with boron gives rise to fluoboric acid gas; and by the union of calcium and oxygen lime is generated, which combines with boracic acid, and is left in the retort as borate of lime. Fluoboric acid gas, therefore, is composed of boron and fluorine. Those who adopt the theory of Gay-Lussac give a different explanation, and regard this gas as a compound of fluoric and boracic acids. The lime of fluor-spar is supposed to unite with one portion of boracic acid, and fluoric acid at the moment of separation with another, yielding borate of lime and fluoboric acid gas.

Prop.—It is a colourless gas, has a penetrating pungent odour, and extinguishes flame on the instant. Its sp. gr. according to Thomson, is 2·3622. It reddens litmus paper as powerfully as sulphuric acid, and forms salts with alkalies which are called *fluoborates*. It has a singularly great affinity for water. When mixed with air or any gas which contains watery vapour, a dense white cloud, a combination of water and fluoboric acid, appears, thus affording an extremely delicate test of the presence of moisture in gases. Water acts powerfully on this gas, absorbing, according to Dr. Davy, 700 times its volume, during which the water increases in temperature and volume. The solution is limpid, fuming, and very caustic. On the application of heat, part of the gas is disengaged; but afterwards the whole solution is distilled.

Gay-Lussac and Thenard and Dr. Davy were of opinion that fluoboric acid gas is dissolved by water without decomposition; but Berzelius denies the accuracy of their observation. On transmitting the gas into water until the liquid acquires a sharply sour taste, but is far from being saturated, a white powder begins to subside; and, on cooling, a considerable quantity of boracic acid is deposited in crystals. It appears that in a certain state of dilution, part of the fluoboric acid and water mutually decompose each other, with formation of boracic and hydrofluoric acids. The latter unites, according to Berzelius, with undecomposed fluoboric acid, forming what he has called *boro-hydrofluoric acid.* On concentrating the liquid by evaporation, the boracic and hydrofluoric acids decompose each other, and the original compound is re-produced.

Fluoboric acid gas does not act on glass, but attacks animal and vegetable matters with energy, converting them like sulphuric acid into a carbonaceous substance. This action is most probably owing to its affinity for water.

When potassium is heated in fluoboric acid gas, the metal takes fire, and a chocolate-coloured solid, wholly devoid of metallic lustre, is formed. This substance is a mixture of boron and fluoride of potassium, from which the latter is dissolved by water, and the boron is left in a solid state.

The composition of fluoboric acid gas has not hitherto been determined by direct experiment. Dr. Davy ascertained that it unites with an equal measure of ammoniacal gas, forming a solid salt; and that it also combines with twice and three times its volume of ammonia, yielding liquid compounds. In the former salt the relative weights of the constituent gases are in the ratio of their specific gravities; and if the compound consists of one equivalent of each, it will be constituted of,

Fluoboric acid gas . .	2·3622 .	68·04 one eq.
Ammoniacal gas . .	0·5898 .	17 one eq.

so that the equivalent of the acid may be assumed in round numbers to be 68. Now supposing this acid to be formed of three eqs. of fluorine and one of boron, its eq. will be 64·04, a number which approximates to the preceding. This view is consistent with the composition of boracic as given at page 263, and with the conversion of fluoboric acid by water into hydrofluoric and boracic acids.

Its symb. is $B + 3F$, or BF_3.

Fluosilicic Acid.—Prep.—This gas is formed whenever hydrofluoric and silicic acids come in contact; and hence pure hydrofluoric acid can be prepared in metallic vessels only, and with fluorspar that is free from rock crystal. The most convenient method of procuring it is to mix in a retort one part of pulverized fluor-spar with its own weight of sand or pounded glass, and two parts of strong sulphuric acid. On applying a gentle heat, fluosilicic acid gas is disengaged with effervescence, and may be collected over mercury.

The chemical changes attending this process are differently explained, according to the view which is taken concerning the nature of the product. In regarding fluor-spar as a compound of fluoric acid and lime, the former at the moment of being set free is thought to unite directly with silicic acid, thereby giving rise to a compound of silicic and fluoric acids. But for reasons already stated, fluor-spar is not considered as fluate of lime; and therefore this view cannot be admitted. It is inferred, on the contrary, that when, by the action of sulphuric acid on fluoride of calcium, hydrofluoric acid is generated, the elements of this acid react on those of silicic acid, and give rise to the production of water and fluosilicic acid gas. This gas is therefore a fluoride of silicon. It may occur to some whether hydrofluoric acid does not unite directly with silicic acid; but this idea is inconsistent with the proportion in which the elements of the gas are found to be united.

Prop.—It is a colourless gas which extinguishes flame, destroys animals that are immersed in it, and irritates the respiratory organs powerfully. It does not corrode glass vessels provided they are quite dry. When mixed with atmospheric air it forms a white cloud, owing to the presence of watery vapour. Its sp. gr. according to Thomson, is 3·6111; and 100 cubic inches of it at 60°, and when the barometer stands at 30 inches, weigh 111·985 grains.

Water acts powerfully on fluosilicic acid gas, of which it condenses, according to Dr. Davy, 365 times its volume (Phil. Trans. for 1812). The gas suffers decomposion at the moment of contact with water, silicic acid in the form of a gelatinous hydrate being deposited, which when well washed is quite pure. The liquid, which has a sour taste and reddens litmus paper, contains the whole of the hydrofluoric acid, together with two-thirds of the silicic acid which was originally present in the gas (Berzelius). By conducting fluosilicic acid gas into a solution of ammonia, complete decomposition ensues:—hydrofluoric acid unites with the alkali, forming hydrofluate of ammonia, and all the silicic acid is deposited. On this fact is founded the mode of analyzing fluosilic acid gas adopted by Dr. Davy and Thomson.

The solution which is formed by fully saturating water with fluosilicic acid gas is powerfully acid, and emits fumes on exposure to the air. It is commonly known by the name of *silicated fluoric acid;* but a more appropriate term is *silico-hydrofluoric acid.* According to the experiments of Berzelius, it appears to be a definite compound of hydrofluoric and silicic acids in the ratio of 3 eqs. of the former to two of the latter. If evaporated before separation from the silicic acid deposited by the action of water on fluosilicic acid gas, this compound is reproduced. But if the solution is poured off from the silicic acid thus deposited, and then evaporated, fluosilicic acid gas is at first evolved, and subsequently hydrofluoric acid and water are expelled. The evaporation of silico-hydrofluoric acid *in vacuo* is attended by a similar change, so that this acid cannot be obtained free from water. It does not corrode glass ; but when evaporated in glass vessels, the production of free hydrofluoric acid of course gives rise to corrosion.

On neutralizing silico-hydrofluoric acid with ammonia, and gently evaporating to dryness, all the silicic acid is rendered insoluble. By exactly neutralizing with carbonate of potassa, a sparingly soluble double fluoride of silicon and potassium subsides ; the precipitation is still more complete with chloride of barium, when the insoluble fluoride of silicon and barium is generated. A variety of similar compounds may be obtained either by double decomposition, or by the action of silico-hydrofluoric acid on metallic oxides.

Its eq. is 78·58 ; symb. $Si + 3F$, or SiF_3.

ON THE COMPOUNDS OF THE SIMPLE NON-METALLIC ACIDIFIABLE COMBUSTIBLES WITH EACH OTHER.

SECTION I.

HYDROGEN AND NITROGEN.—AMMONIACAL GAS.

Hist. and Prep.—The aqueous solution of ammonia, under the name of *spirit of hartshorn*, has been long known to chemists ; but its existence as a gas was first noticed by Priestley, who described it in his works under the title of *alkaline air.* It is often called the *volatile alkali ;* but the terms ammonia and ammoniacal gas are now usually employed. Although a product of the decomposition of organic substances, it has been thought better to describe it here, from its great importance in inorganic chemistry.

An abundant supply of ammoniacal gas may be obtained from any salt of ammonia by the action of a pure alkali or alkaline earth; but hydrochlorate of ammonia and lime, from economical considerations, are always employed. The proportions to which I give the preference are equal parts of hydrochlorate of ammonia and well-burned quicklime, considerable excess of lime being taken, in order to decompose the hydrochlorate more expeditiously and completely. The lime is slaked by the addition of water; and as soon as it has fallen into powder, it should be placed in an earthen pan and be covered till it is quite cold, in order to protect it from the carbonic acid of the air. It is then mixed in a mortar with the hydrochlorate of ammonia, previously reduced to a fine powder; and the mixture is put into a retort or other convenient glass vessel. Heat is then applied, and the temperature gradually increased as long as free evolution of gas continues. The residue consists of chloride of calcium and lime.

The gas, thus liberated, must be collected over mercury, as it is most rapidly absorbed by water. Advantage is taken of this property to prepare what is commonly though incorrectly termed liquid ammonia. For this purpose a current of gas is transmitted into distilled water, which is kept cool by means of ice or moist cloths, and the process is continued as long as any gas is absorbed. A highly concentrated solution of ammonia is thus obtained. The most convenient method of preparing ammoniacal gas for purposes of experiment is by applying a gentle heat to the concentrated solution, contained in a glass vessel. It soon enters into ebullition, and a large quantity of pure ammonia is disengaged.

Prop.—Ammonia is a colourless gas, which has a strong pungent odour, and acts powerfully on the eyes and nose. It is quite irrespirable in its pure form, but when diluted with air, it may be taken into the lungs with safety. Burning bodies are extinguished by it, nor is the gas inflamed by their approach. Ammonia, however, is inflammable in a low degree; for when a lighted candle is immersed in it, the flame is somewhat enlarged, and tinged of a pale yellow colour at the moment of being extinguished; and a small jet of the gas will burn in an atmosphere of oxygen. A mixture of ammoniacal and oxygen gases detonates by the electric spark; water being formed, and nitrogen set free. A little nitric acid is generated at the same time, except when a smaller quantity of oxygen is employed than is sufficient for combining with all the hydrogen of the ammonia. (Henry, Phil. Trans. 1809.)

Ammoniacal gas at the temperature of 50° and under a pressure equal to 6·5 atmospheres, becomes a transparent colourless liquid. It is also liquefied, according to Guyton-Morveau, under the common pressure, by a cold of —70°; but there is no doubt that the liquid which he obtained was a solution of ammonia in water.

It has all the properties of an alkali in a very marked manner. Thus it has an acrid taste, and gives a brown stain to turmeric paper; though the yellow colour soon reappears on exposure to the air, owing to the volatility of the alkali. It combines also with acids, and neutralizes their properties completely. All these salts suffer decomposition by being heated with the fixed alkalies or alkaline earths, such as potassa or lime, the union of which with the acid of the salt causes the separation of its ammonia. None of the ammoniacal salts can sustain a red heat without being dissipated in vapour or decomposed, a character which manifestly arises from the volatile nature of the alkali. If combined with a volatile acid, such as the hydrochloric, the compound itself sublimes unchanged by heat; but when united with an acid, which is fixed at a low red heat, such as the phosphoric, the ammonia alone is expelled. It is here considered that the salts of ammonia are formed by its direct union with acids. Another, and a very scientific view, has been adopted by Berzelius. When an electric current is passed through a weak solution of ammonia, it is decomposed by the secondary action, hydrogen from decomposed water being evolved at the negative electrode and nitrogen at the positive (Faraday, Phil. Trans. 1834). But if a portion of mercury form the negative electrode, no hydrogen is evolved, and the mercury is rapidly converted into a light porous substance, which has the lustre and all the characters of an amalgam. As soon as it is removed from the influence of the electric current, rapid decomposition ensues, mercury is reproduced, and hydrogen and ammoniacal gases are evolved in the ratio of one measure of the former to two of the latter, according to the observations of Gay-Lussac and Thenard. The production of this compound is explained by Berzelius on the supposition that ammonia by uniting with an additional eq. of hydrogen forms a compound, which has all the properties of a metal; he therefore calls it ammonium. The oxide of ammonium, the composition of which is represented by the formula $NH_4 + O$, he considers to be the base of the ammoniacal salts. This view is supported by several facts, which will be considered when treating of the salts.

Hydrogen and nitrogen gases do not unite directly, and therefore chemists have no synthetic proof of the constitution of ammonia. Its composition, however, has been determined analytically with great exactness. When a succession of electric sparks is passed through ammoniacal gas, it is resolved into its elements; and the same effect is produced by conducting it through porcelain tubes heated to redness. A. Berthollet analyzed ammonia in both ways, and ascertained that 200 measures of that gas, on being decomposed, occupy the space of 400 measures, 300 of which are hydrogen, and 100 nitrogen. Henry has made an analysis of ammonia by means of electricity, and his experiment proves beyond a doubt that the proportions above given are rigidly exact. (Annals of Philosophy, xxiv. 346.)

	Grains.
Now since 150 cubic inches of hydrogen weigh .	3·205
and 50 of nitrogen . . .	15·083
100 cubic inches of ammonia must weigh .	18·288

and it is composed by weight of

Hydrogen . .	3·205	3 .	or 3 equivalents.
Nitrogen . .	15·083	14·15 .	or 1 equivalent.

The sp. gr. of ammonia, according to this calculation, is 0·5898, a number which agrees closely with those ascertained directly by Davy and Thomson.

Ammoniacal gas has a powerful affinity for water. Owing to this attraction, a piece of ice, when introduced into a jar full of ammonia, is instantly liquefied, and the gas disappears in the course of a few seconds. Davy, in his Elements, stated that water at 50°, and when the barometer stands at 29·8 inches, absorbs 670 times its volume of ammonia, and that the solution has a sp. gr. of 0·875. According to Thomson, water at the common temperature and pressure takes up 780 times its bulk. By strong compression, water absorbs the gas in still greater quantity. Heat is evolved during its absorption; and a considerable expansion, independently of the increased temperature, occurs at the same time.

The concentrated solution of ammonia is a clear colourless liquid, of sp. gr. 0·936. It possesses the peculiar pungent odour, taste, alkalinity, and other properties of the gas itself. On account of its great volatility it should be preserved in well-stopped bottles, a measure which is also required to prevent the absorption of carbonic acid. At a temperature of 130° it enters into ebullition, owing to the rapid escape of pure ammonia; but the whole of the gas cannot be expelled by this means, as at last the solution itself evaporates. It freezes at about the same temperature as mercury.

The following table, from Davy's Elements of Chemical Philosophy, shows the quantity of real ammonia contained in 100 parts of solutions of different sp. gravities at 59° F. and when the barometer stands at 30 inches. The sp. gr. of water is supposed to be 10,000:—

Table of the quantity of real Ammonia in solutions of different densities.

100 parts of sp. gravity.		Of real Ammonia.	100 parts of sp. gravity.		Of real Ammonia.
8750	contain	32·5	9435	contain	14·53
8875		29·25	9476		13·46
9000		26·00	9513		12·40
9054		25·37	9545		11·56
9166		22·07	9573		10·82
9255		19·54	9597		10·17
9326		17·52	9619		9·60
9385		15·88	9692		9·50

The presence of free ammoniacal gas may always be detected by its odour, by its temporary action on yellow turmeric paper, and by its forming dense white fumes, hydrochlorate of ammonia, when a glass rod moistened with hydrochloric acid is brought near it.

Besides ammonia and ammonium, another compound of nitrogen and hydrogen is believed to exist, the composition of which is represented by the formula, NH_2. It is only known in combination, and has been named *Amide*. Its compounds, which are important, will be described in treating of organic chemistry.

Its eq. is 17·15; eq. vol. $= 200$; symb. $N + 3H$, or NH_3.

SECTION II.

COMPOUNDS OF HYDROGEN AND CARBON.

CHEMISTS have for several years been acquainted with two distinct compounds of carbon and hydrogen, viz. carburetted hydrogen and olefiant gases; but late researches have enriched the science with several other compounds of a similar nature, to which much interest is attached. They are remarkable for their number, for supplying some instructive instances of isomerism, and for their tendency to unite with and even neutralize powerful acids, without, in their uncombined state, manifesting any ordinary signs of alkalinity. Several of them are particularly distinguished by their chemical affinities; for although compound, they exhibit in their combinations with other substances the characteristics of an element. They have hence been called the compound radicals. These compound radicals are closely associated both with the organic and inorganic chemistry. In the latter they must hold a place, as being compounds formed by the direct union of two elements; and in the former they are the roots or radicals of the various organic products.

Light Carburetted Hydrogen.—Hist.—This gas is sometimes called *heavy inflammable air*, the *inflammable air of marshes*, and *hydrocarburet*. Agreeably to the principles of chemical nomenclature, taking carbon as the electro-negative element, it is a *dicarburet of hydrogen;* but it is generally termed *light carburetted hydrogen.* It is formed abundantly in stagnant pools during the spontaneous decomposition of dead vegetable matter; and it may readily be procured by stirring the mud at the bottom of them, and collecting the gas, as it escapes, in an inverted glass vessel. In this state it is found to contain 1-20th of carbonic acid gas, which may be removed by means of lime water or a solution of pure potassa, and 1-15th or 1-20th of nitrogen. This is the only convenient method of obtaining it.

Prop—Colourless, tasteless, nearly inodorous; always gaseous when uncombined; does not change the colour of litmus or turmeric paper. Water, according to Henry, absorbs about 1-60th of its volume. It extinguishes all burning bodies, and is unable to support the respiration of animals. It is highly inflammable; and when a jet of it is set on fire, it burns with a yellow flame, and with a much stronger light than is occasioned by hydrogen gas. With a due proportion of atmospheric air or oxygen gas it forms a mixture which detonates powerfully with the electric spark, or by the contact of flame. The sole products of the explosion are water and carbonic acid.

Dalton first ascertained the real nature of light carburetted hydrogen; and it has since been particularly examined by Thomson, Davy, and Henry. When 100 measures are detonated with rather more than twice their volume of oxygen gas, the whole of the inflammable gas and precisely 200 measures of the oxygen disappear, water is condensed, and 100 measures of carbonic acid are produced. Now 100 measures of carbonic acid gas contain (page 235) 100 of carbon vapour and 100 of oxygen gas, just half the oxygen which had been employed; and the remaining oxygen requires 200 measures of hydrogen to form water. Hence as, at 60° F. and 30 inches Bar.,

		Grains.
100	cubic inches of carbon vapour weigh	13·153
200	do. hydrogen gas	4·2636
100	do. light carburetted hydrogen must weigh	17·4166

These weights are obviously in the ratio of 2 to 6·12, as already assigned; and the sp. gr. of such a gas ought to be 0·5594, which is nearly the quantity found experimentally by Thomson and Henry.

Light carburetted hydrogen is not decomposed by electricity, nor by being passed through red-hot tubes, unless the temperature is very intense, in which case some of the gas does suffer decomposition, each volume yielding two volumes of pure hydrogen gas and a deposite of charcoal. Mixed with chlorine, no action takes place at common temperatures, when quite dry, even if exposed to the direct solar rays. If moist, and the mixture is kept in a dark place, still no action ensues: but if light be admitted, particularly sunshine, decomposition follows. The nature of the products depends upon the proportion of the gases. If four measures of chlorine and one of light carburetted hydrogen are present, carbonic and hydrochloric acid gases will be produced: two volumes of chlorine combine with two volumes of hydrogen contained in the carburetted hydrogen, and the other two volumes of chlorine decompose so much water as will likewise give two volumes of hydrogen, forming hydrochloric acid; while the oxygen of the water unites with the carbon, and converts it into carbonic acid. If there are three instead of four volumes of chlorine, carbonic oxide will be generated instead of carbonic acid, because one-half less water will be decomposed (Henry). If a mixture of chlorine and light carburetted hydrogen is electrified or exposed to a red heat, hydrochloric acid is formed, and charcoal deposited.

Its eq. is 8·12; eq. vol. = 100; symb. H_2C.

It was first ascertained by Henry (Nicholson's Journal, vol. xix.); and his conclusions have been fully confirmed by the subsequent researches of Davy, that the *fire-damp* of coal-mines consists almost solely of light carburetted hydrogen. This gas often issues in large quantity from between beds of coal, and by collecting in mines, owing to deficient ventilation, gradually mingles with atmospheric air, and forms an explosive mixture. The first unprotected light which then approaches, sets fire to the whole mass, and an explosion ensues. These accidents, which were formerly so frequent and so fatal, are now comparatively rare, owing to the employment of the safety-lamp. For this invention we are indebted to Davy, who established the principles of its construction by a train of elaborate experiment and close reasoning, which may be regarded as one of the happiest efforts of his genius (Essay on Flame).

Davy commenced the inquiry by determining the best proportion of air and light carburetted hydrogen for forming an explosive mixture. When the inflammable gas is mixed with 3 or 4 times its volume of air, it does not explode at all. It detonates feebly when mixed with 5 or 6 times its bulk of air, and powerfully when 1 to 7 or 8 is the proportion. With 14 times its volume, it still forms a mixture which is explosive; but if a larger quantity of air be admitted, a taper burns in it only with an enlarged flame.

The temperature required for causing an explosion was next ascertained. It was found that the strongest explosive mixture may come in contact with iron or other solid bodies heated to redness, or even to whiteness, without detonating, provided they are not in a state of actual combustion; whereas the smallest point of flame, owing to its higher temperature, instantly causes an explosion.

The last important step in the inquiry was the observation that flame cannot pass through a narrow tube. This led to the discovery, that the power of tubes in preventing the transmission of flame is not necessarily connected with any particular length; and that a very short one will have the effect, provided its diameter is proportionally reduced. Thus, a piece of fine wire gauze, which may be regarded as an assemblage of short narrow tubes, is quite impermeable to flame; and consequently, if a common oil lamp be completely surrounded with a cage of such gauze, it may be introduced into an explosive atmosphere of fire-damp and air, without kindling the mixture. This simple contrivance, which is appropriately termed the *safety-lamp*, not only prevents explosion, but indicates the precise moment of danger. When the lamp is carried into an atmosphere charged with fire damp, the flame begins to enlarge; and the mixture, if highly explosive, takes fire as soon as it has passed through the gauze, and burns on its inner surface, while the light in the centre of the lamp is extinguished. Whenever this appearance is observed, the miner must instantly withdraw; for though the flame should not be able to communicate with the explosive mixture on the outside of the lamp, as long as the texture of the gauze remains entire, yet the heat emitted during the combustion is so great, that the wire, if exposed to it for a few minutes, would suffer oxidation, and fall to pieces.

The peculiar operation of small tubes in obstructing the passage of flame admits of a very simple explanation. Flame is gaseous matter heated so intensely as to be luminous; and Davy has shown that the temperature necessary for producing this effect is far higher than the white heat of solid bodies. Now, when flame comes in contact with the sides of very minute apertures, as when wire gauze is laid upon a burning jet of coal gas, it is deprived of so much heat that its temperature instantly falls below the degree at which gaseous matter is luminous; and consequently, though the gas itself passes freely through the interstices, and is still very hot, it is no longer incandescent. Nor does this take place when the wire is cold only; —the effect is equally certain at any degree of heat which the flame can communicate to it. For since the gauze has a large extent of surface, and from its metallic nature is a good conductor of heat, it loses heat with great rapidity. Its temperature, therefore, though it may be heated to whiteness, is always so far below that of flame, as to exert a cooling influence over the burning gas, and reduce its heat below the point at which it is incandescent.

These principles suggest the conditions under which Davy's lamp would cease to be safe. If a lamp with its gauze red-hot be exposed to a *current* of explosive mixture, the flame may possibly pass so rapidly as not to be cooled below the point of ignition, and in that case an accident might occur with a lamp which would be quite safe in a calm atmosphere. It has been lately shown by Messrs. Upton and Roberts, lamp manufacturers of this city, that flame may in this way be made to pass through the safety-lamp as commonly constructed; and I am satisfied, from having witnessed some of their experiments, that the observation is correct. This then may account for accidents in coal-mines where the safety-lamp is constantly employed. An obvious mode of avoiding such an evil is to diminish the apertures of the gauze; but this remedy is nearly impracticable from the obstacle which very fine gauze causes to the diffusion of light. A better method is to surround the common safety-lamp with a glass cylinder, allowing air to enter solely at the bottom of the lamp through wire gauze of extreme fineness, placed horizontally, and to escape at top by a similar contrivance. Upton and Roberts have constructed a lamp of this kind, through which I have in vain tried to cause the communication of flame, and which appears to me perfectly secure: should an accident break the glass, their lamp would be reduced to a safety lamp of the common construction. Davy's lamp thus modified gives a much better light than without the glass, just as all lamps burn better with a shade than without one.

The compound commonly called olefiant gas, which contains 2 eq. carbon and 2 eq. hydrogen, will be described in the organic chemistry, among the compounds of acetate, the organic radical of acetic acid.

The other compounds of carbon and hydrogen are also described in the organic chemistry. They belong to this department not only as being products of the organic kingdom, but also on account of their atomic constitution; for whenever they are acted on by chlorine or any other dehydrodizing agents, one part of the hydrogen, which enters into their composition, is shown to be in a state of combination different from the rest. Thus evidence is obtained that these compounds, although composed of nothing but hydrogen and carbon, are not formed by the direct union of these elements, but that a portion of the hydrogen with the carbon forms a compound radical, which acts the part of an element and combines as such with the remainder of the hydrogen.

SECTION III.

COMPOUNDS OF HYDROGEN AND SULPHUR.

Sulphur unites with hydrogen in at least two proportions, and the resulting compounds are thus constituted :—

	Hydrogen.	Sulphur.	Equiv.	Formulæ.
Hydrosulphuric acid	1 1 eq.+	16·1 1 eq. =	17·1	HS.
Persulphuret of hydrogen	1 1 eq.+	32·2 2 eq. =	33·2	HS_2.

Hydrosulphuric Acid.—Hist. and Prep.—Commonly known under the name of sulphuretted hydrogen. It is best prepared by heating sesquisulphuret of antimony in a retort, or other convenient glass vessel, with four or five times its weight of strong hydrochloric acid; when, by an interchange of elements, sesquichloride of antimony and hydrosulphuric acid are generated, the latter of which escapes with effervescence. The elements concerned before and after the change, are

1 eq. Sesquisulphuret of antimony and 3 eq. Hydrochloric acid
Sb_2S_3 $3HCl$.

which yield

3 eq. Hydrosulphuric acid and 1 eq. Sesquichloride of antimony.
$3HS$ Sb_2Cl_3

It may also be formed by the action of sulphuric acid diluted with 3 or 4 parts of water on protosulphuret of iron: this sulphuret and water interchange elements, hydrosulphuric acid and protoxide of iron are generated, and the latter unites with sulphuric acid, while the former in the state of gas is rapidly disengaged. Hydrochloric acid may be substituted for the sulphuric. A sulphuret of iron may be procured for the purpose, either by igniting common iron pyrites, by which means nearly half of its sulphur is expelled, or by exposing to a low red heat a mixture of two parts of iron filings and rather more than one part of sulphur. The materials should be placed in a common earthen or cast-iron crucible, and be protected as much as possible from the air during the process. The sulphuret procured from iron filings and sulphur always contains some uncombined iron, and therefore the gas obtained from it is never quite pure, being mixed with a little free hydrogen. This, however, for many purposes, is immaterial.

Prop.—Colourless gas, which reddens moist litmus paper feebly, and is distinguished from all other gaseous substances by its offensive taste and odour, which is similar to that of putrefying eggs, or the water of sulphurous springs. Under a pressure of 17 atmospheres, at 50°, it is compressed into a limpid liquid, which resumes the gaseous state as soon as the pressure is removed. To animal life it is very injurious. According to Dupuytren and Thenard, the presence of 1-1500th of this gas in air is instantly fatal to a small bird; 1-1000th killed a middle-sized dog; and a horse died in an atmosphere which contained 1-250th of its volume.

It extinguishes all burning bodies; but the gas takes fire when a lighted candle is immersed in it, and burns with a pale blue flame. Water and sulphurous acid are the products of its combustion, and sulphur is deposited. With oxygen gas it forms a mixture which detonates by the application of flame or the electric spark: if 100 measures of it are exploded with 150 of oxygen, the former is completely consumed, the oxygen disappears, water is deposited, and 100 measures of sulphurous acid gas remain (Thomson). From the result of this experiment, the composition of hydrosulphuric acid gas may be inferred; for it is clear, from the composition of sulphurous acid (page 244), that two-thirds of the oxygen must have combined with sulphur; and, therefore, that the remaining one-third contributed to the formation of water. Consequently, hydrosulphuric acid contains its own volume of hydrogen gas, and 16·66 of the vapour of sulphur; and since

	Grains.
16·66 cubic inches of the vapour of Sulphur weigh	34·361
100 cubic inches of Hydrogen gas weigh	2·1318
100 cubic inches of Hydrosulp. acid gas must weigh	36·4928

The sp. gr. of a gas so constituted should be 1·177, which agrees with observation; and its elements are in the ratio of 1 to 16·1, as already mentioned.

The accuracy of this view is confirmed by several circumstances. Thus, according to Gay-Lussac and Thenard, the weight of 100 cubic inches of hydrosulphuric acid gas is 36·33 grains. When sulphur is heated in hydrogen gas, hydrosulphuric acid is generated without any change of volume. On igniting platinum wires in it by means of the voltaic apparatus, sulphur is deposited, and an equal volume of pure hydrogen remains; and a similar effect is produced, though more slowly, by a succession of electric sparks (Elements of Davy, p. 282). Gay-Lussac and Thenard found that on heating tin in hydrosulphuric acid gas, sulphuret of tin is formed; and when potassium is heated in it, vivid combustion ensues, with formation of sulphuret of potassium. In both cases, pure hydrogen is left, which occupies precisely the same space as the gas from which it was derived. (Recherches Physico-Chimiques, vol. i.)

The salts of hydrosulphuric acid are called *hydrosulphates*, and sometimes *hydrosulphurets*. This acid, however, rarely unites directly with metallic oxides; but in most cases its hydrogen combines with the oxygen of the oxide and its sulphur with the metal. All the hydrosulphates which do exist are decomposed by sulphuric or hydrochloric acids, and hydrosulphuric acid gas is disengaged with effervescence.

Recently boiled water absorbs its own volume of hydrosulphuric acid, becomes thereby feebly acid, and acquires the peculiar odour and taste of sulphurous springs. The gas is expelled without change by boiling the water.

The elements of hydrosulphuric acid may easily be separated from one another. A solution of the gas cannot be preserved in an open vessel, because its hydrogen unites with the oxygen of the atmosphere, and sulphur is deposited. When mixed with sulphurous acid, both compounds are decomposed, water is generated, and sulphur set free. On pouring into a bottle of the gas a little fuming nitric acid, mutual decomposition ensues, a bluish-white flame frequently appears, sulphur and nitrous acid fumes come into view, and water is generated. Chlorine, iodine, and bromine decompose it, with separation of sulphur, and formation of hydrochloric, hydriodic, and hydrobromic acids. An atmosphere charged with hydrosulphuric acid gas may be purified by means of chlorine in the space of a few minutes.

Hydrosulphuric acid gas is readily distinguished from other gases by its odour, by tarnishing silver with which it forms a sulphuret, and by the character of the precipitate which it produces with solutions of arsenious acid, tartar emetic, and salts of lead. The most delicate test of its presence, when diffused in the air, is moist carbonate of oxide of lead spread on white paper.

Its eq. is 17·1; eq. vol. = 100; symb. HS.

Persulphuret of Hydrogen.—Hist. and Prep.—Discovered by Scheele, but first specially described by Berthollet (An. de Chimie, xxv.). When protosulphuret of potassium (or of any metal of the alkalies and alkaline earths) is mixed in solution with sulphuric acid, the oxygen of water unites with potassium and its hydrogen with sulphur, just as when protosulphuret of iron is employed, hydrosulphuric acid and sulphate of potassa being generated: the elements K + S and H + O mutually interchange, and yield K + O and H + S. If the potassium be combined with two or more equivalents of sulphur as in the so called *liver of sulphur* made by fusing carbonate of potassa with half of its weight of sulphur, then one of two events will happen: the hydrogen of the decomposed water will either unite with 1 eq. of sulphur and form hydrosulphuric acid, the superfluous sulphur subsiding in the form of a grey hydrate, or with 2 eqs. of sulphur, and give rise to persulphuret of hydrogen. Now, the former of these changes always occurs when the acid is added to the persulphuret of potassium;

and the latter takes place when a concentrated solution of that sulphuret is added by little and little to the acid, provided the acid is in considerable excess, and the mixture well stirred after each addition. The same phenomena ensue when hydrochloric instead of sulphuric acid is employed; but then there are two sources from which hydrogen may be supplied. It may be derived, as above, from decomposed water, hydrochlorate of potassa being generated; or hydrochloric acid itself may be decomposed, its hydrogen uniting with sulphur and its chlorine with potassium. On all such occasions I adopt the latter view, and will give reasons for doing so in the section introductory to the study of the metals.

Such are the principles to be attended to in preparing persulphuret of hydrogen. In practice it is conveniently made by boiling equal parts of recently slaked lime and flowers of sulphur with 5 or 6 parts of water for half an hour, when a deep orange-yellow solution is formed, which contains persulphuret of calcium. Let this liquid be filtered, and gradually added cold to an excess of hydrochloric acid diluted with about twice its weight of water, briskly stirring. A copious deposit of sulphur falls (the sulphur præcipitatum of the London Pharmacopœia), and persulphuret of hydrogen gradually subsides in the form of a yellowish semi-fluid matter like oil. The change which ensues in the formation of the yellow solution may be theoretically represented thus:—

2 eq. lime & 6 eq. sulphur yield 1 eq. hyposulph. acid & 2 eq. bisulphuret calcium.
$2CaO+S_6$ yield $S_2O_2+2CaS_2$.

The hyposulphurous acid exists in solution united with lime, and is decomposed when hydrochloric acid is added, resolving itself into sulphurous acid and sulphur; a change not essentially connected with the production of persulphuret of hydrogen, but resulting from the mode of preparing the persulphuret of calcium. It is probable that the calcium is combined with more than 2 eqs. of sulphur, and that the deposited sulphur is derived from that source as well as from decomposed hyposulphurous acid.

Prop.—From the facility with which this substance resolves itself into sulphur and hydrosulphuric acid, its history is imperfect: we are indebted to an essay by Thenard for the principal facts which are known (An. de Ch. et Ph. xlviii. 79). At common temperatures it is a viscid liquid, of a yellow colour, with a density of about 1·769, and a consistence varying between that of a volatile and fixed oil. It has the peculiar odour and taste of hydrosulphuric acid, though in a less degree. Its elements are so feebly united, that in the cold it gradually resolves itself into sulphur and hydrosulphuric acid, and suffers the same change instantly by a heat considerably short of 212° F. Decomposition is also produced by the contact of most substances, especially of metals, metallic oxides, even the alkalies, and metallic sulphurets. Thus effervescence from the escape of hydrosulphuric acid gas is produced by peroxide of manganese, silica, the alkaline earths in powder, and solutions of potassa or soda; and the oxides of gold and silver are reduced by it with such energy, that they are rendered incandescent. It is remarkable that the substance which causes the decomposition often undergoes no chemical change whatever. In these respects persulphuret of hydrogen bears a close analogy to peroxide of hydrogen; and Thenard has traced other points of resemblance. They are both, for instance, rendered more stable by the presence of acids; they both whiten the tongue and skin when applied to them, and they are both possessed of bleaching properties.

The composition of persulphuret of hydrogen has been variously stated. According to Dalton it is a bisulphuret, consisting of two equivalents of sulphur and one of hydrogen; and this view of its composition is corroborated by Sir John Herschel's analysis of persulphuret of calcium (Edin. Phil. Journal, i. 13). But Thenard found its constituents to vary; whence it is probable that hydrogen is capable of uniting with sulphur in several proportions.

Persulphuret of hydrogen is sometimes regarded as an acid; and on this supposition it may be termed *hydropersulphuric acid*, and its salts *hydropersulphates.* This view is founded on the hypothesis, that the solutions formed by boiling lime or an alkali with sulphur contain hyposulphite and hydropersulphate of lime, the hydrogen in the one acid and oxygen in the other being attributed to decomposed water, and not hyposulphite of lime and persulphuret of calcium, as I have supposed. The latter view is more consistent with the fact that persulphuret of hydrogen in its free state has no acidity, and exhibits no tendency to unite with alkalies.

Its eq. is $= 33{\cdot}2$; symb. $H\,S_2$.

SECTION IV.

HYDROGEN AND SELENIUM.—HYDROSELENIC ACID.

Selenium, like sulphur, forms a gaseous compound with hydrogen, which has distinct acid properties, and is termed *seleniuretted* *hydrogen*, or *hydroselenic acid*. It is disengaged by the action of dilute sulphuric or hydrochloric acid on a protoseleniuret of any of the more oxidable metals, such as potassium, calcium, manganese, or iron, the explanation being the same as in the formation of hydrosulphuric acid from protosulphuret of iron.

Hydroselenic acid gas is colourless. Its odour is at first similar to that of hydrosulphuric acid; but it afterwards irritates the lining membrane of the nose powerfully, excites catarrhal symptoms, and destroys for some hours the sense of smelling. It is absorbed freely by water, forming a colourless solution, which reddens litmus paper, and gives a brown stain to the skin. The acid is soon decomposed by exposure to the atmosphere; for the oxygen of the air unites with the hydrogen of the hydroselenic acid, and selenium, in the form of a red powder, subsides. It is decomposed by nitric acid and chlorine in the same manner as hydrosulphuric acid; and, like that gas, it decomposes many metallic salts, the hydrogen of the acid combining with the oxygen of the oxide, while an insoluble seleniuret of the metal is generated.

According to the analysis of Berzelius, hydroselenic acid consists of 39·6 parts or 1 eq. of selenium, and 1 part or 1 eq. of hydrogen: so that its eq. is 40·6; its symb. HSe.

SECTION V.

COMPOUNDS OF HYDROGEN AND PHOSPHORUS.

The existence of two compounds of phosphorus and hydrogen, the phosphuretted and perphosphuretted hydrogen, have, until lately, been generally admitted by chemists. Their composition and properties have been closely studied by Dumas, Buff, Rose, and Graham (An. de Ch. et Ph. xxxi. 113; xli. 220; and xli. 5. Phil. Mag. v. 401). The investigations of these chemists concurred in proving that phosphuretted hydrogen consists of 31·4 parts or 2 eqs. of phosphorus, and 3 parts or 3 eqs. of hydrogen; while the discordancy in their analyses of perphosphuretted hydrogen, caused great uncertainty respecting its constitution. Thus, although Dumas and Rose agree that 100 measures of perphosphuretted hydrogen contain 150 measures of hydrogen, the former states that 1 part of hydrogen is united with 15·9 of phosphorus, the latter with 10·52, while Thomson estimates the quantity at 12. The result of Rose would indicate that the two compounds of phosphorus and hydrogen are isomeric, being identical in composition, and differing in character only by the one being spontaneously inflammable, and the other not so. The accuracy of the analytical results of Rose have been recently established by the discoveries of Leverrier (An. de Ch. et Ph. lx. 174), who has proved that perphosphuretted hydrogen is a mixture of phosphuretted hydrogen with about $\frac{1}{30}$ of its volume of a spontaneously inflammable compound, which he considers to be composed of 31·4 parts or 2 eqs. of phosphorus, and 2 parts or 2 eqs. of hydrogen. In the same paper he establishes the existence of a compound formed of 31·4 parts or 2 eqs. of phosphorus, and 1 part or 1 eq. of hydrogen. The compounds of phosphorus and hydrogen are therefore,

	Phos.	Hyd.	Equiv.	Formulæ.
Solid Phosphuretted Hydrogen .	31·4 2 eq. +	1 1 eq. =	32·4	P_2H.
Inflammable ditto. .	31·4 2 eq. +	2 2 eq. =	33·4	P_2H_2.
Gaseous . ditto. .	31·4 2 eq. +	3 3 eq. =	34·4	P_2H_3.

Solid Phosphuretted Hydrogen.—When phosphuretted hydrogen gas, recently prepared by the action of quick-lime and phosphorus, is exposed in the moist state to a strong diffused light, or to the direct rays of the sun, the solid phosphuretted hydrogen is deposited on the sides of the glass vessel. It is also left as an insoluble powder when phosphuret of potassium is dissolved in water. As obtained by the former process, it is a canary yellow flocculent matter, is insoluble in water and alcohol; but with the former, a slow oxidation takes place, and hydrogen is evolved. It is not altered by a temperature of 234°, but heated beyond that point it is decomposed. When brought into contact with chlorine and nitric acid, it suffers instantaneous decomposition. According to the analysis of Leverrier, it is composed of 1 part or 1 eq. of hydrogen, and 31·4 parts or 2 eqs. of phosphorus. Hence its eq. is 32·4; symb. HP_2.

PHOSPHURETTED HYDROGEN.

Hist. and Prep.—Discovered by Davy in 1812. It may be prepared by several methods. Davy prepared it by heating hydrated phosphorous acid in a retort (page 256); and it is evolved from hydrous hypophosphorous acid by similar treatment, and by the action of strong hydrochloric acid on phosphuret of calcium according to Dumas. It may also be obtained, but in an impure state, by boiling phosphorus with a solution of potassa or milk of lime. Its production is in these cases dependent on the decomposition of water, the oxygen and hydrogen of which unite with different portions of phosphorus, and phosphoric acid, hypophosphorous acid and phosphuretted hydrogen are generated.

Prop.—A transparent colourless gas of an exceedingly offensive odour and bitter taste. It has no action on test paper. It is absorbed in small quantity by water, but freely by solutions of chloride of calcium or sulphate of the oxide of copper, by which means its purity may be ascertained. Like sulphuretted hydrogen, it frequently decomposes metallic salts, giving rise to the formation of water and a phosphuret of the metal. But if the metal have a feeble affinity for oxygen, it is thrown down in the metallic state, and water and phosphoric acid are generated. This is the case, according to Rose, with solutions of gold and silver.

It is a non-supporter of combustion, and is very destructive to animal life. When pure, it may be mixed with air or oxygen gas at common temperatures without danger; but the mixture detonates with the electric spark, or at a temperature of 300°. Even diminished pressure causes an explosion ; an effect which, in operating with a mercurial trough, is produced simply by raising the tube, so that the level of the mercury within may be a few inches higher than at the outside. Such is the property of the pure gas, as obtained from the hydrated phosphorous or hypophosphorous acids ; but if it be procured from the action of phosphorus on potassa or hydrate of lime, it is remarkable for being spontaneously inflammable when mixed with air or oxygen gas. If the beak of the retort from which it issues is plunged under water, so that successive bubbles of the gas may arise through the liquid, a very beautiful appearance takes place. Each bubble, on reaching the surface of the water, bursts into flame, and forms a ring of dense white smoke, which enlarges as it ascends, and retains its shape, if the air is tranquil, until it disappears. The wreath is formed by the products of the combustion—metaphosphoric acid and water. If received in a vessel of oxygen gas, the entrance of each bubble is instantly followed by a strong concussion, and a flash of white light of extreme intensity. It is remarkable that whatever may be the excess of oxygen, traces of phosphorus always escape combustion ; but that if the gas be previously mixed with three times its volume of carbonic acid, and be then mixed with oxygen, the combustion is perfect. Dalton observed that it may be mixed with pure oxygen in a tube three-tenths of an inch in diameter without taking fire; but that the mixture detonates when an electric spark is transmitted through it.

In consequence of the combustibility of phosphuretted hydrogen, it would be hazardous to mix it in any quantity with air or oxygen gas in close vessels. For the same reason care is necessary in the formation of this gas, lest, in mixing with the air of the apparatus, an explosion ensue, and the vessel burst. The risk of such an accident is avoided, when phosphuret of calcium is used, by filling the flask or retort entirely with dilute acid; and in either of the other processes, by causing the phosphuretted hydrogen to be formed slowly at first, in order that the oxygen gas within the apparatus may be gradually consumed. A very simple method of averting all danger has been mentioned by Graham. It consists in moistening the interior of the retort with one or two drops of ether, the vapour of which, when mixed with atmospheric air even in small proportion, effectually prevents the combustion of phosphuretted hydrogen. The same effect may be produced by the addition of several other bodies. He also finds that a gas, which is not spontaneously inflammable, acquires this property on being mixed with from $\frac{1}{1000}$ to $\frac{1}{10000}$ of its volume of nitrous acid. According to Leverrier, it is very probable that there exists a compound of phosphorus and hydrogen composed of 2 eqs. of each of its elements, and that this compound being spontaneously inflammable communicates that property to phosphuretted hydrogen gas. This opinion is grounded on the fact that when spontaneously inflammable phosphuretted hydrogen is kept for any length of time in a dark place it suffers no change, but if brought into a strong light solid phosphuretted hydrogen is deposited, and the residual gas is no longer spontaneously inflammable. Thus it appears that by the action of light P_2H_2 is decomposed, and P_2H and P_2H_3 are formed. The result of his analysis supports this view.

Dumas ascertained the composition of phosphuretted hydrogen by introducing into a tube containing the gas a fragment of bichloride of mercury, and applying heat so as to convert it into vapour. Mutual decomposition instantly took place: phosphuret of mercury and hydrochloric acid were generated; and 100 measures of gas, thus decomposed, yielded 300 measures of hydrochloric acid gas, corresponding to 150 of hydrogen. The quantity of hydrogen contained in any given volume of phosphuretted hydrogen is thus found; and the weight of the former deducted from that of the latter gives the quantity of combined phosphorus. This inference is conformable to the quantity of oxygen required for the combustion of phosphuretted hydrogen. Thomson affirms that when this gas is detonated with 1·5 of its volume of oxygen gas, the only products are water and phosphorous acid; but that when the oxygen is in considerable excess, two volumes disappear for one of the compound, and water and phosphoric acid are generated. Now the hydrogen contained in one volume of phosphuretted hydrogen is equal to 1·5, and it unites with 0·75 of oxygen. Hence if 0·75, or $\frac{3}{4}$, be deducted from 1·5 and from 2, the remainders, $\frac{3}{4}$ and $\frac{5}{4}$, represent the relative quantity of oxygen which is required to convert the same weight of phosphorus into phosphorous and phosphoric acid. These numbers are obviously in the ratio of 3 to 5, as already stated on the authority of Berzelius (page 254). The elements of the calculation have been confirmed both by Dumas and Buff.

Agreeably to these views, and to the combining volume of phosphorus (page 174), 100 measures of phosphuretted hydrogen gas contain 150 of hydrogen gas and 25 of the vapour of phosphorus; and hence, as

			Grains.
150	cubic inches of	Hydrogen gas weigh	3·1977
25	do.	Phosphorous vapour weigh	33·5425
100	do.	Phosphuretted Hydrogen gas should weigh . .	36·7402.

The calculated density of a gas so constituted should be 1·1853, which is nearly a mean of the observations of Dumas and Rose.

If the equivalent of phosphorus were 31·4 instead of 15·7, as is very far from improbable, then the combining volume of phosphorus vapour would be 50 instead of 25 (page 174); and phosphuretted hydrogen would consist of 50 measures of phosphorous vapour and 150 of hydrogen gas condensed into 100 measures, thus agreeing in composition with ammoniacal gas.

Phosphuretted hydrogen has neither an acid nor alkaline reaction; but in its chemical relations it inclines to alkalinity. Thus it unites with hydrobromic and hydriodic acids, forming definite compounds which crystallize in cubes; and Rose finds that it unites with metallic chlorides, forming compounds analogous to those which ammonia forms with metallic chlorides.

Its eq. is 34·4; eq. vol. = 100; symb. $2P + 3H$, or P_2H_3.

SECTION VI.

COMPOUNDS OF NITROGEN AND CARBON.

BICARBURET OF NITROGEN, OR CYANOGEN GAS.

Hist. and Prep.—Discovered in 1815 by Gay-Lussac (An. de Ch. xcv.). It is prepared by heating carefully dried bicyanuret of mercury in a small glass retort by means of a spirit lamp. This cyanuret, which was formerly considered a compound of oxide of mercury and prussic acid, and was then called *prussiate of mercury*, is composed of metallic mercury and cyanogen. On exposure to a low red heat it is resolved into its elements; the cyanogen passes over in the form of gas, and the metallic mercury is sublimed. The retort, at the close of the process, contains a small residue of a dark brown matter like charcoal, but which Johnston has shown to consist of the same ingredients as the gas itself.

Prop.—A colourless gas possessing a strong pungent and very peculiar odour. At the temperature of 45° and under a pressure of 3·6 atmospheres, it is a limpid liquid, which Kemp finds to be a non-conductor of electricity, and which resumes the gaseous form when the pressure is removed. It extinguishes burning bodies; but it is inflammable, and burns with a beautiful and characteristic purple flame. It can support a strong heat without decomposition. Water at the temperature of 60° absorbs 4·5 times, and alcohol 23 times its volume of the gas. The aqueous solution reddens litmus paper; but this effect is not to be ascribed to the gas itself, but to the presence of acids which are generated by the mutual decomposition of cyanogen and water. It appears from the observations of Wöhler that two of the products are cyanic acid and ammonia; which, uniting together, generate urea (An. de Ch. et Ph. xliii. 73).

The composition of cyanogen may be determined by mixing that gas with a due proportion of oxygen, and inflaming the mixture by electricity. Gay-Lussac ascertained in this way that 100 measures of cyanogen require 200 of oxygen for complete combustion, that no water is formed, and that the products are 200 measures of carbonic acid gas and 100 of nitrogen. Hence it follows that cyanogen contains its own bulk of nitrogen, and twice its volume of the vapour of carbon. Consequently, since

		Grains.
100 cubic inches of Nitrogen gas weigh	. . . .	30·166
200 do. the vapour of Carbon weigh	. . .	26·306
100 cubic inches of Cyanogen gas must weigh	. . .	56·472

The ratio of its elements by weight is,

Nitrogen	30·166	0·9727		14·15	1 eq.
Carbon	26·306	0·8430	(2+0·4215)	12·24	2 eq.

The sp. gr. of a gas so constituted is $0·9727 + 0·843 = 1·8157$, which is near 1·8064, the number found experimentally by Gay-Lussac.

Cyanogen is a *bicarburet of nitrogen*, the formula of which is $N + 2C$, or NC_2; but its most convenient name is *cyanogen*, proposed by its discoverer,* which may be expressed shortly by Cy. Its eq. is 26·39.

Paracyanogen.—An examination of the brown matter, left in the retort after the preparation of cyanogen gas, has been made by Johnston, who by burning it with chlorate of potassa found it to contain carbon and nitrogen united in the same ratio as in cyanogen gas. It is, in fact, a solid bicarburet of nitrogen, isomeric with cyanogen, but differing from it essentially in its physical and chemical relations. On heating this solid bicarburet in the open air, several definite compounds of carbon and nitrogen may be successively obtained. After considerable heating, the ratio of carbon to nitrogen is as 3 to 2; again heated, the proportion becomes as 7 to 6; and finally, after a still longer heat, the ratio of the equivalents is as 1 to 1. Thus the carbon is gradually burned away, leaving the nitrogen fixed, until a protocarburet of nitrogen is formed. On continuing the heat after this period, both elements fly off together, and the whole is dissipated. The solid bicarburet of cyanogen is also generated, when a saturated solution of cyanogen in alcohol is kept in contact with mercury; and Johnston suggests that the carbonaceous residue after the charring of animal substances by heat, is probably in many cases a carburet of nitrogen, and not pure charcoal as is commonly thought. (Brewster's Journ. N.S. i. 75.) Paracyanogen is soluble in sulphuric and nitric acids, and forms a compound with oxygen in which 1 eq. of oxygen is combined with 4 eqs. of nitrogen and 8 eqs. of carbon. Hence the eq. of paracyanogen is probably 105·56, and its symb. N_4C_8.

---

* From κυανος, *blue*, and γενναω, *I generate*; because it is an essential ingredient of Prussian blue.

Mellon—Is obtained when sulphuret of cyanogen, melame, melamine, ammeline, or ammelide, is exposed to a red heat. It is a lemon yellow powder, is insoluble in water and alcohol, but is dissolved and decomposed by acids and alkalies. Exposed to a strong red heat, it is decomposed and forms 1 vol. of nitrogen and 3 vols. of cyanogen gas. It is one of the compound radicals. Its eq. is 93·32; symb. N_4C_6. (*Lieb. An.* ix. 5.)

Cyanogen, though a compound body, has a remarkable tendency to combine with elementary substances. Thus it is capable of uniting with the simple non-metallic bodies, and evinces a strong attraction for metals. When potassium, for instance, is heated in cyanogen gas, such energetic action ensues, that the metal becomes incandescent, and cyanuret of potassium is generated. The affinity of cyanogen for metallic oxides, on the contrary, is comparatively feeble. It enters into direct combination with a few alkaline bases only, and these compounds are by no means permanent. From these remarks it is apparent that cyanogen has no claim to be regarded as an acid, as it has none of the properties of a compound. It is, in fact, a compound radical of organic chemistry, and therefore its various combinations will be described in that part of the work.

SECTION VII.

COMPOUND OF PHOSPHORUS AND NITROGEN.

Phosphuret of Nitrogen.—First described by Rose (Pogg. An. xxviii. 529). On saturating either of the chlorides of phosphorus with dry ammoniacal gas, a white solid mass is obtained, which on exposure to a strong red heat gives rise to the formation of phosphuret of nitrogen, hydrochloric acid gas being at the same time evolved. It is also formed when the vapour of either chlorides of phosphorus are brought into contact with sal-ammonia heated nearly to its point of sublimation.

It is a light snow-white powder; is insoluble in water, and in dilute acid, or alkaline solutions. It is not changed by a red heat in close vessels, or in an atmosphere of chlorine, or the vapour of sulphur; but in hydrogen it is decomposed with the formation of ammoniacal gas. It is composed of 31·4 parts or 2 eqs. of phosphorus, and 14·15 parts or 1 eq. of nitrogen.

Its eq. is 45·55; symb. $N+2P$, or NP_2.

SECTION VIII.

COMPOUND OF SULPHUR, CARBON, ETC.

The compounds described in this section are thus constituted :—

Bisulph. of Carbon	Carb. 6·12 + Sulp. 32·2=38·32.	C+2 S	CS_2.
Sulph. of Phosphorus	Composition uncertain.		
Bisulph. of Selenium	Selen. 39·6 + Sulp. 32·2=71·8.	Se+2 S	SeS_2.
Seleni. of Phosphorus	Composition uncertain.		

Bisulphuret of Carbon.—Hist.—This substance was discovered accidentally in the year 1796 by Professor Lampadius, who regarded it as a compound of sulphur and hydrogen, and termed it *alcohol of sulphur*. Clément and Desormes first declared it to be a sulphuret of carbon, and their statement was fully confirmed by the joint researches of Berzelius and the late Dr. Marcet (Phil. Trans. 1813).

Prep. — Bisulphuret of carbon may be obtained by heating in close vessels native bisulphuret of iron (iron pyrites) with one-fifth of its weight of well-dried charcoal; or by transmitting the vapour of sulphur over fragments of charcoal heated to redness in a tube of porcelain. The compound, as it is formed, should be conducted by means of a glass tube into cold water, at the bottom of which it is collected. To free it from moisture and adhering sulphur, it should be distilled at a low temperature in contact with chloride of calcium.

Prop.—It is a transparent colourless liquid, which is remarkable for its high refractive power. Its sp. gr. is 1·272; of its vapour, 2·668. It has an acid, pungent, and somewhat aromatic taste, and a very fetid odour. It is exceedingly volatile; its vapour at 63·5° supports a column of mercury 7·36 inches long; and at 110° it enters into brisk ebullition. From its great volatility it may be employed for producing intense cold. It is very inflammable, and kindles in the open air at a temperature scarcely exceeding that at which mercury boils. It burns with a pale blue flame. Admitted into a vessel of oxygen gas, so much vapour rises as to form an explosive mixture; and when mixed in like manner with binoxide of nitrogen, it forms a combustible mixture, which is kindled on the approach of a lighted taper, and burns rapidly, with a large greenish-white flame of dazzling brilliancy. It dissolves readily in alcohol and ether, and is precipitated from the solution by water. It dissolves sulphur, phosphorus, and iodine, and the solution of the latter has a beautiful pink colour. Chlorine decomposes it, with formation of chloride of sulphur. The pure acids have little action upon it. By nitro-hydrochloric acid it is changed into a white crystalline substance like camphor, which Berzelius regards as a compound of the hydrochloric, carbonic, and sulphurous acids.

Bisulphuret of carbon is a sulphur-acid, that is, unites with *sulphur-bases* to constitute compounds analogous to ordinary salts, and hence called *sulphur-salts.* Thus bisulphuret of carbon unites with sulphuret of potassium, forming a sulphur-salt, in which the former acts as an acid and the latter as a base. The same compound is formed by the action of bisulphuret of carbon on a solution of pure potassa: but in this case sulphuret of potassium is first generated by an interchange of elements with a portion of bisulphuret of carbon, carbonic acid being produced at the same time. Thus—

2 eq. potassa & 1 eq. bisulph. carbon yield 2 eq. sulphuret potassium and 1 eq. carb. acid.
$2KO+CS_2$ $2KS+CO_2$.

If the bisulphuret of carbon is in sufficient quantity, carbonic acid gas is disengaged, and a neutral compound results. Such is inferred to be the nature of the change, agreeably to the researches of Berzelius on the sulphur-salts.

Its eq. is 38·32; eq. vol. $=100$; symb. CS_2.

Sulphuret of Phosphorus.—When sulphur and fused phosphorus are brought into contact they unite readily, but in proportions which have not been precisely determined; and they frequently react on each other with such violence as to cause an explosion. For this reason the experiment should be made with a quantity of phosphorus not exceeding 30 or 40 grains. The phosphorus is placed in a glass tube, 5 or 6 inches long, and about half an inch wide; and when by a gentle heat it is liquefied, the sulphur is added in successive small portions. Heat is evolved at the moment of combination, and hydrosulphuric and phosphoric acids, owing to the presence of moisture, are generated. This compound may also be made by agitating flowers of sulphur with fused phosphorus under water. The temperature should not exceed 160°; for otherwise hydrosulphuric and phosphoric acids would be evolved so freely as to prove dangerous, or at least to interfere with the success of the process.

Sulphuret of phosphorus, from the nature of its elements, is highly combustible. It is much more fusible than phosphorus. A compound made by Faraday with about 5 parts of sulphur and 7 of phosphorus, was quite fluid at 32°, and did not solidify at 20° (Quarterly Journal, iv.).

Bisulphuret of Selenium.—Sulphur and selenium mix together in all proportions by fusion, and therefore by such means it is difficult to procure a definite compound; but the bisulphuret of an orange colour was formed by Berzelius by precipitating a solution of selenious acid with hydrosulphuric acid. The sulphuret found by Stromeyer among the volcanic products of the Lipari isles is probably similar in composition. Bisulphuret of selenium fuses at a heat a little above 212°, and at a higher temperature may be sublimed without change. In the open air it takes fire when heated, and sulphurous, selenious, and selenic acids are the products of its combustion. The alkalies and soluble metallic sulphurets dissolve it. Nitric acid acts upon it with difficulty; but the nitro-hydrochloric converts it into sulphuric and selenious acids. (An. of Phil. xiv.)

Seleniuret of Phosphorus.—This compound may be prepared in the same manner as the sulphuret of phosphorus; but as selenium is capable of uniting with phosphorus in several proportions, the compound formed by fusing them together can hardly be supposed to be of a definite nature. This seleniuret is very fusible, sublimes without change in close vessels, and is inflammable. It decomposes water gradually when digested in it, giving rise to seleniuretted hydrogen, and one of the acids of phosphorus.

Sulphuret of Nitrogen.—This compound is formed, according to Soubeiran, by the action of water on a compound of chloride of sulphur and ammonia, $SCl + 2NH_3$. The sulphuret of nitrogen is a yellow or green solid, the colour of which varies according to the mode of preparation. It is converted, by digestion with water, entirely into hyposulphurous acid and ammonia; hence its composition is NS_3 and $2NS_3 + 6HO = 2NH_3 + 3S_2O_2$.

When aqua ammoniæ acts on chloride of sulphur a red solid compound is formed, which is composed of chloride of sulphur, sulphuret of nitrogen, and ammonia. This body undergoes spontaneous decomposition, and is converted into a yellow pulverulent mass (Soubeiran). When this mass, which consists chiefly of sulphur, is boiled with alcohol, or exhausted by percolation with cold alcohol, the alcohol dissolves a substance in small quantity, which may be had in white needles or cubical crystals, and which contains 92 — 93 p. c. sulphur and 5 — 6 p. c. nitrogen. Gregory, who discovered this compound, thought that it might be a sulphuret of nitrogen. But in its analysis he always obtained a little hydrogen, and the nature of this substance was left unsettled. Soubeiran is of opinion that it contains sulphur, nitrogen, and ammonia. The quantity of sulphur, however, is so large, that its constitution must be unusual; and it merits a careful examination. Gregory showed that its solution in alcohol, when mixed with an alcoholic solution of caustic potash, acquires a deep amethyst colour, which soon disappears, while ammonia is set free, pure hyposulphite of potash is deposited, and traces of a volatile compound, probably formed at the expense of the alcohol, are observed.

METALS.

GENERAL PROPERTIES OF METALS.

Metals are distinguished from other substances by the following properties. They are all conductors of electricity and heat. When the compounds which they form with oxygen, chlorine, iodine, sulphur, and similar substances, are submitted to the action of galvanism, the metals always appear at the negative side of the battery, and are hence said to be positive electrics. They are quite opaque, refusing a passage to light, though reduced to very thin leaves. They are in general good reflectors of light, and possess a peculiar lustre, which is termed the metallic lustre.—Every substance in which these characters reside may be regarded as a metal.

The number of metals, the existence of which is admitted by chemists, amounts to forty-two. The following table contains the names of those that have been procured in a state of purity, together with the date at which they were discovered, and the names of the chemists by whom the discovery was made.

Table of the Discovery of Metals.

Names of Metals.	Authors of the Discovery.	Dates of the Discovery.
Gold Silver Iron Copper Mercury Lead Tin	Known to the Ancients.	
Antimony	Described by Basil Valentine	1490
Bismuth	Described by Agricola in	1530
Zinc	First mentioned by Paracelsus	16th century
Arsenic Cobalt	Brandt, in	1733
Platinum	Wood, assay-master, Jamaica	1741
Nickel	Cronstedt	1751
Manganese	Gahn and Scheele	1774
Tungsten	D'Elhuyart	1781
Tellurium	Müller	1782
Molybdenum	Hielm	1782
Uranium	Klaproth	1789
Titanium	Gregor	1791
Chromium	Vauquelin	1797

Table of the Discovery of Metals—(continued).

Names of Metals.	Authors of the Discovery.	Dates of the Discovery.
Columbium	Hatchett	1802
Palladium	Wollaston	1803
Rhodium		
Iridium	Descotils and Smithson Tennant	1803
Osmium	Smithson Tennant	1803
Cerium	Hisinger and Berzelius	1804
Potassium	Davy	1807
Sodium		
Barium		
Strontium		
Calcium		
Cadmium	Stromeyer	1818
Lithium	Arfwedson	1818
Zirconium	Berzelius	1824
Aluminium	Wöhler	1828
Glucinium		
Yttrium		
Thorium	Berzelius	1829
Magnesium	Bussy	1829
Vanadium	Sefström	1830
Lantanium	Mosander	1839

Most of the metals are remarkable for their great sp. gravity; some of them, such as gold or platinum, which are the densest bodies known in nature, being more than 19 times heavier than an equal bulk of water. Great density was once supposed to be an essential characteristic of metals; but the discovery of potassium and sodium, which are so light as to float on the surface of water, has shown that this supposition is erroneous. Some metals experience an increase of density to a certain extent when hammered, their particles being permanently approximated by the operation. On this account, the density of some of the metals contained in the following table is represented as varying between two extremes.

Table of the Specific Gravity of Metals at 60° Fahr. compared to Water as Unity.

Platinum	20·98	Brisson.
Gold	19·257	Do.
Tungsten	17·6	D'Elhuyart.
Mercury	13·568	Brisson.
Palladium	11·3 to 11·8	Wollaston.
Lead	11·352	Brisson.
Silver	10·474	Do.
Bismuth	9·822	Do.
Uranium	9·000	Bucholz.
Copper	8·895	Hatchett.
Cadmium	8·604	Stromeyer.
Cobalt	8·538	Haüy.
Arsenic	5·8843	Turner.
Nickel	8·279	Richter.
Iron	7·788	Brisson.

Molybdenum	7·400	Hielm
Tin	7·291	Brisson
Zinc	6·861 to 7·1	Do.
Manganese	6·850	Bergmann
Antimony	6·702	Brisson
Tellurium	6·115	Klaproth
Titanium	5·3	Wollaston
Sodium	0·972	Gay-Lussac and Thenard.
Potassium	0·865	

Some metals possess the property of *malleability*, that is, admit of being beaten into thin plates or leaves by hammering. The malleable metals are gold, silver, copper, tin, platinum, palladium, cadmium, lead, zinc, iron, nickel, potassium, sodium, and frozen mercury. The other metals are either malleable in a very small degree only, or, like antimony, arsenic, and bismuth, are actually brittle. Gold surpasses all metals in malleability: one grain of it may be extended so as to cover about 52 square inches of surface, and to have a thickness not exceeding $\frac{1}{282020}$th of an inch.

Nearly all malleable metals may be drawn out into wires, a property which is expressed by the term *ductility*. The only metals which are remarkable in this respect are gold, silver, platinum, iron, and copper. Wollaston devised a method by which gold wire may be obtained so fine that its diameter shall be only $\frac{1}{5000}$th of an inch, and that 550 feet of it are required to weigh one grain. He obtained a platinum wire so small, that its diameter did not exceed $\frac{1}{30000}$th of an inch (Phil. Trans. 1813). It is singular that the ductility and malleability of the same metal are not always in proportion to each other. Iron, for example, cannot be made into fine leaves, but it may be drawn into very small wires.

The tenacity of metals is measured by ascertaining the greatest weight which a wire of a certain thickness can support without breaking. According to the experiments of Guyton-Morveau, whose results are comprised in the following table, iron, in point of tenacity, surpasses all other metals.

The diameter of each wire was 0·787th of a line.

	Pounds.
Iron wire supports	549·25
Copper	302·278
Platinum	274·32
Silver	187·137
Gold	150·753
Zinc	109·54
Tin	34·63
Lead	27·621

According to some recent observations of Baudrimont, the process of annealing destroys the tenacity of metals to a considerable extent. Thus he found that a wire of soft iron which supported a weight of 26 lbs., on being annealed could only bear 12 lbs.; and a copper wire which could support 22 lbs. was broken, when annealed, by 9 lbs. Numerous experiments with different specimens of brass wire confirm the generality of the result (An. de Ch. et Ph. lx. 78).

Metals differ also in hardness; but I am not aware that their exact relation to each other, under this point of view, has been determined by experiment. In the list of hard metals may be placed titanium, manganese, iron, nickel, copper, zinc, and palladium. Gold, silver, and platinum are softer than these; lead is softer still, and potassium and sodium yield to the pressure of the fingers. The properties of elasticity and sonorousness are allied to that of hardness. Iron and copper are in these respects the most conspicuous.

Many of the metals have a distinctly crystalline texture. Iron, for example, is fibrous; and zinc, bismuth, and antimony are lamellated. Metals are sometimes obtained also in crystals; and most of them in crystallizing assume the figure of a cube, the regular octohedron, or some form allied to it. Gold, silver, and copper occur naturally in crystals; while others crystallize when they pass gradually from the liquid to the solid condition. Crystals are most readily procured from those metals which fuse at a low temperature; and bismuth, from conducting heat less perfectly than other metals, and therefore cooling more slowly, is best fitted for the purpose. The process should be conducted in the way already described for forming crystals of sulphur.

Metals, with the exception of mercury, are solid at common temperatures; but they may all be liquefied by heat. The degree at which they *fuse*, or their *point* of *fusion*, is very different for different metals, as appears from the following table:—

Table of the Fusibility of different Metals.

		Fahr.	
Fusible below a red heat.	Mercury . .	—39°	Different chemists.
	Potassium . .	136	Gay-Lussac and Thenard.
	Sodium . .	190	
	Tin .	442	Crichton.
	Bismuth . .	497	
	Lead . .	612	
	Tellurium—rather less fusible than lead		Klaproth.
	Arsenic—undetermined.		
	Zinc . . .	773	Daniell.
	Antimony—a little below a red heat.		
	Cadmium . about	442	Stromeyer.

Table of the Fusibility of different Metals, continued.

Infusible below a red heat.	Silver . . .	1873	Daniell.	
	Copper . . .	1996		
	Gold . . .	2016		
	Cobalt—rather less fusible than iron.			
	Iron, cast . .	2786	Daniell.	
	Iron, malleable .	Requiring the highest heat of a smith's forge.		
	Manganese . .			
	Nickel—nearly the same as cobalt.			
	Palladium.			
	Molybdenum	Almost infusible, and not to be procured in buttons by the heat of a smith's forge.		Fusible before the oxy-hydrogen blowpipe.
	Uranium			
	Tungsten .			
	Chromium			
	Titanium	Infusible in the heat of a smith's forge, but fusible before the oxy-hydrogen blowpipe.		
	Cerium			
	Lantanium			
	Osmium			
	Iridium			
	Rhodium			
	Platinum			
	Columbium			

Metals differ also in volatility. Some are readily volatilized by heat, while others are of so fixed a nature that they may be exposed to the most intense heat of a wind furnace without being dissipated in vapour. There are seven metals, the volatility of which has been ascertained with certainty; namely, cadmium, mercury, arsenic, tellurium, potassium, sodium, and zinc.

Metals cannot be resolved in to more simple parts; and therefore, in the present state of chemistry, they must be regarded as elementary bodies. It was formerly conceived that they might be converted into each other; and this notion led to the vain attempts of the alchemists to convert the baser metals into gold. The chemist has now learned that his art solely consists in resolving compound bodies into their elements, and causing substances to unite which were previously uncombined. One elementary principle cannot assume the properties peculiar to another.

Metals have an extensive range of affinity, and on this account few of them are found in the earth *native*, that is, in an uncombined form. They commonly occur in combination with other bodies, especially with oxygen and sulphur, in which state they are said to be *mineralized*. It is a singular fact in the chemical history of the metals, that they are little disposed to combine in the metallic state with compound bodies, such as an oxide or an acid. They unite readily, on the contrary, with elementary substances. Thus they often combine with each other, yielding compounds termed *alloys*, which possess all the characteristic physical properties of pure metals. They unite likewise with the simple non-metallic substances, such as oxygen, chlorine, and sulphur, giving rise to new bodies in which the metallic character is wholly wanting. In all these combinations the same tendency to unite in a few definite proportions, is equally conspicuous as in that department of the science of which I have just completed the description. The chemical changes are regulated by the same general laws, and in describing them the same nomenclature is applicable.

The order which it is proposed to follow in describing the metals has already been explained in the introduction; but before treating of each separately, some general observations may be premised, by which the study of this subject will be much facilitated.

Metals are of a combustible nature, that is, they are not only susceptible of slow oxidation, but, under favourable circumstances, they unite rapidly with oxygen, giving rise to all the phenomena of real combustion. Zinc burns with a brilliant flame when heated to full redness in the open air; iron emits vivid scintillations on being inflamed in an atmosphere of oxygen gas; and the least oxidable metals, such as gold and platinum, scintillate in a similar manner when heated by the oxy-hydrogen blowpipe.

The product either of the slow or rapid oxidation of a metal, when heated in the air, has an earthy aspect, and was called a *calx* by the older chemists, the process of forming it being expressed by the term *calcination*. Another method of oxidizing metals is by *deflagration*; that is, by mixing them with nitrate or chlorate of potassa, and projecting the mixture into a red-hot crucible. Most metals may be oxidized by digestion in nitric acid; and nitro-hydrochloric acid is an oxidizing agent of still greater power.

Some metals unite with oxygen in one proportion only, but most of them have two or three degrees of oxidation. Metals differ remarkably in their relative forces of attraction for oxygen. Potassium and sodium, for example, are oxidized by mere exposure to the air; and they decompose water at all temperatures the instant they come in contact with it. Iron and copper may be preserved in dry air without change, nor can they decompose water at common temperatures; but they are both slowly oxidized by exposure to a moist atmosphere, and combine rapidly with oxygen when heated to redness in the open air. Iron has a stronger affinity for oxygen than copper; for the former decomposes water at a red heat, whereas the latter cannot produce that effect. Mercury is less inclined than copper to unite with oxygen. Thus it may be exposed without change to the influence of a moist atmosphere. At a temperature of 650° or 700° it is oxidized; but at a red heat it is reduced to the metallic state, while oxide of copper can sustain the strongest heat of a blast furnace without losing its oxygen. The affinity of gold for oxygen is still weaker than that of mercury; for it will bear the most intense heat of our furnaces without oxidation.

Metallic oxides suffer *reduction*, or may be reduced to the metallic state in several ways:

1. By heat alone. By this method the oxides of gold, silver, mercury, and platinum may be decomposed.

2. By the united agency of heat and combustible matter. Thus, by transmitting a current of hydrogen gas over the oxides of copper or iron heated to redness in a tube of porcelain, water is generated, and the metals are obtained in a pure form. Carbonaceous matters are likewise used for the purpose with great success. Potassa and soda, for example, may be decomposed by exposing them to a white heat after being intimately mixed with charcoal in fine powder. A similar process is employed in metallurgy for extracting metals from their ores, the inflammable materials being wood, charcoal, coke, or coal. In the more delicate operations of the laboratory, charcoal, *black flux*, and formiate of soda are preferred.

3. By the galvanic battery. This is a still more powerful agent than the preceding; since some oxides, such as baryta and strontia, which resist the united influence of heat and charcoal, are reduced by the agency of galvanism.

4. By the action of deoxidizing agents on metallic solutions. Phosphorous acid, for example, when added to a liquid containing oxide of mercury, deprives the oxide of its oxygen, metallic mercury subsides, and phosphoric acid is generated. Formic acid and formiate of soda, when boiled with the solutions of the oxides of gold, platinum, silver, mercury, &c. reduces the metals. In like manner, one metal may be precipitated by another, provided the affinity of the latter for oxygen exceeds that of the former. Thus, when mercury is added to a solution of nitrate of the oxide of silver, metallic silver is thrown down, and oxide of mercury is dissolved by the nitric acid. On placing metallic copper in the liquid, pure mercury subsides, and a nitrate of the oxide of copper is formed; and from this solution metallic copper may be precipitated by means of iron.

Metals, like the simple non-metallic bodies, may give rise to oxides or acids by combining with oxygen. The former are the most frequent products. Many metals which are not acidified by oxygen may be formed into oxides; whereas one metal only, arsenic, is capable of forming an acid and not an oxide. All the other metals which are convertible into acids by oxygen, such as chromium, tungsten, and molybdenum, are also susceptible of yielding one or more oxides. In these instances, the acids always contain a larger quantity of oxygen than the oxides of the same metal.

Many of the metallic oxides have the property of combining with acids. In some instances all the oxides of a metal are capable of forming salts with acids, as is exemplified by the oxides of iron; but, generally, the protoxide is the sole *alkaline* or *salifiable base.* Most of the metallic oxides are insoluble in water; but all those that are soluble have the property of giving a brown stain to yellow turmeric paper, and of restoring the blue colour of reddened litmus.

Oxides sometimes unite with each other, and form definite compounds. The most abundant ore of chromium, commonly called chromate of iron, is an instance of this kind; and the red oxide of manganese, the magnetic oxide of iron, and the red oxide of lead, appear to belong to the same class of bodies.

Chlorine has a powerful affinity for metallic substances. It combines readily with most metals at common temperatures, and the action is in many instances so violent as to be accompanied with the evolution of light. For example, when powdered zinc, arsenic, or antimony is thrown into a jar of chlorine gas, the metal is instantly inflamed. The attraction of chlorine for metals even surpasses that of oxygen. Thus, when chlorine is brought into contact at a red heat with pure lime, magnesia, baryta, strontia, potassa, or soda, oxygen is emitted, and a chloride of the metal is generated, the elements of which are so strongly united that no temperature hitherto tried can separate them. All other metallic oxides are, with few exceptions, acted on in the same manner by chlorine, and in some cases the change takes place below the temperature of ignition.

Most of the metallic chlorides are solid at common temperatures. They are fusible by heat, assume a crystalline texture in cooling, and under favourable circumstances crystallize with regularity. Several of them, such as the chlorides of tin, arsenic, antimony, and mercury, are volatile, and may be sublimed without change. They are for the most part colourless, do not possess the metallic lustre, and have the aspect of a salt. Two of the chlorides are insoluble in water, namely, chloride of silver and protochloride of mercury; several, such as the chlorides of antimony, arsenic, and titanium, are decomposed by that liquid; but most of them are more or less soluble.

Some of the metallic chlorides, those especially of gold and platinum, are decomposable by heat. All the chlorides of the common metals are decomposed at a red heat by hydrogen gas, hydrochloric acid being disengaged while the metal is set free. Pure charcoal does not effect their decomposition; but if moisture be present at the same time, hydrochloric and carbonic acid gases are formed, and the metal remains. They resist the action of anhydrous sulphuric acid; but all the chlorides, excepting those of silver and mercury, are readily decomposed by hydrated sulphuric acid, with disengagement of hydrochloric acid gas. The change is accompanied with decomposition of water, the hydrogen of which combines with chlorine, and its oxygen with the metal. When in solution, they may be recognized by yielding with nitrate of oxide of silver a white precipitate, which is chloride of silver.

Metallic chlorides may in most cases be formed by direct action of chlorine on the pure metals. They are also frequently procured by dissolving metallic oxides in hydrochloric acid, evaporating to dryness, and applying heat so long as any water is expelled. Metallic chlorides are often deposited from such solutions by crystallization.

Iodine has a strong attraction for metals; and most of the compounds which it forms with them sustain a red heat in close vessels without decomposition. But in the degree of its affinity for metallic substances it is inferior to chlorine and oxygen. We have seen that chlorine has a stronger affinity than oxygen for metals, since it decomposes nearly all oxides at high temperatures; and it separates iodine also from metals under the same circumstances. If the vapour of iodine is brought into contact with potassa, soda, protoxide of lead, or oxide of bismuth, heated to redness, oxygen gas is evolved, and the metals of those oxides will unite with iodine. But iodine, so far as is known, cannot separate oxygen from any other metal; nay, all the iodides, except those just mentioned, are decomposed by exposure to oxygen gas at the temperature of ignition. All the iodides are decomposed by chlorine, bromine, and concentrated sulphuric and nitric acids; and the iodine which is set free may be recognized either by the colour of its vapour, or by its action on starch. The metallic iodides are generated under circumstances analogous to those above mentioned for procuring the chlorides.

The action of iodine on metallic oxides, when dissolved or suspended in water, is precisely analogous to that of chlorine. On adding iodine to a solution of the pure alkalies or alkaline earths, an iodide and iodate are generated.

Bromine in its affinity for metallic substances is intermediate between chlorine and iodine; for while chlorine disengages bromine from its combination with metals, metallic iodides are decomposed by bromine. The same phenomena attend the union of bromine with metals, as accompany the formation of metallic chlorides. Thus, antimony and tin take fire by contact with bromine, and its action with potassium is attended with a flash of light, and intense heat. These compounds have as yet been but partially examined. They may be formed by the action of bromine on the pure metals, and often by dissolving metallic oxides in hydrobromic acid, and evaporating the solution to dryness. Bromine unites with potassa, soda, and some other oxides, constituting bleaching compounds similar to the chlorides above described. Bromide of lime is obtained by the action of bromine on milk of lime, a yellowish solution being formed with water, which bleaches powerfully.

As fluorine has not hitherto been obtained in a separate state, the nature of its action on the metals is unknown; but the chief difficulty of procuring it in an insulated form appears to arise from its extremely powerful affinity for metallic substances, in consequence of which, at the moment of becoming free, it attacks the vessels and instruments employed in its preparation. The best mode of preparing the soluble fluorides, such as those of potassium and sodium, is by dissolving the carbonate of these alkalies in hydrofluoric acid, and evaporating the solution to perfect dryness. The insoluble fluorides are easily formed by precipitation from the soluble fluorides. They are without exception decomposed by concentrated sulphuric acid with the aid of heat; and the hydrofluoric acid, in escaping, may easily be detected by its action on glass.

Sulphur, like the preceding elementary substances, has a strong tendency to unite with metals, and the combination may be effected in several ways:

1. By heating the metal directly with sulphur. The metal, in the form of powder or filings, is mixed with a due proportion of

sulphur, and the mixture heated in an earthen crucible, which is covered to prevent the access of air; or if the metal can sustain a red heat without fusing, the vapour of sulphur may be passed over it while heated to redness in a tube of porcelain. The act of combination, which frequently ensues below the temperature of ignition, is attended by free disengagement of heat, which in several instances is so great, that the whole mass becomes luminous, and shines with a vivid light. This appearance of combustion, which occurs quite independently of the presence of oxygen, is exemplified by the sulphurets of potassium, sodium, copper, iron, lead, and bismuth.

2. By igniting a mixture of a metallic oxide and sulphur.

3. By depriving the sulphate of an oxide of its oxygen by means of heat and combustible matter. Charcoal or hydrogen gas may be employed for the purpose, as will be described immediately.

4. By hydrosulphuric acid, or a soluble metallic sulphuret. Nearly all the salts of the second class of metals are decomposed when a current of hydrosulphuric acid gas is conducted into their solutions. The salts of uranium, iron, manganese, cobalt, and nickel are exceptions; but these are precipitated by sulphuret of potassium.

The sulphurets are opaque brittle solids, many of which, such as the sulphurets of lead, antimony, and iron, have a metallic lustre. They are all fusible by heat, and commonly assume a crystalline texture in cooling. Most of them are fixed in the fire; but the sulphurets of mercury and arsenic are remarkable for their volatility. All the sulphurets, excepting those of the first class of metals, are insoluble in water.

Most of the protosulphurets support an intense heat without decomposition; but, in general, those which contain more than one equivalent of sulphur, lose part of it when strongly heated. They are all decomposed without exception by exposure to the combined agency of air or oxygen gas and heat; and the products depend entirely on the degree of heat and the nature of the metal. The sulphuret is more or less converted into the sulphate of an oxide, provided the sulphate is able to support the temperature employed in the operation. If this is not the case, the sulphur is evolved under the form of sulphurous acid, and a metallic oxide is left; or if the oxide itself is decomposed by heat, the pure metal remains. The action of heat and air in decomposing metallic sulphurets is the basis of several metallurgic processes. A few sulphurets are decomposed by the action of hydrogen gas at a red heat, the pure metal being set free and hydrosulphuric acid evolved. Rose finds that the only sulphurets which admit of being easily reduced to the metallic state in this way are those of antimony, bismuth, and silver. The sulphuret of tin is decomposed with difficulty, and requires a very high temperature. All the other sulphurets which he subjected to this treatment were either deprived of a part only of their sulphur, such as bisulphuret of iron, or were not attacked at all, as happened with the sulphurets of zinc, lead, and copper. (Poggendorff's Annalen, iv. 109.)

Many of the metallic sulphurets were formerly thought to be compounds of sulphur and a metallic oxide; an error first pointed out by Proust, who demonstrated that protosulphuret of iron, as well as the bisulphuret, are compounds of sulphur and metallic iron without any oxygen. (Journal de Physique, liii.) He proved the same of the sulphurets of other metals, such as mercury and copper. He was of opinion, however, that in some instances sulphur does unite with a metallic oxide. Thus, when sulphur and peroxide of tin are heated together, sulphurous acid is disengaged, and the residue according to Proust is a sulphuret of the protoxide, but in this he was in error.

In 1817 Vauquelin extended these views to the compounds formed by heating an alkali or an alkaline earth with sulphur, which were previously regarded as sulphurets of a metallic oxide. He explained that the elements of the alkali unite with separate portions of sulphur, forming a metallic sulphuret and sulphuric acid, the latter of which unites with undecomposed alkali. Thus, in preparing the so-called *liver of sulphur*, made by fusing carbonate of potassa with sulphur, one portion of the alkali is completely decomposed, its elements unite separately with sulphur, giving rise to sulphuret of potassium and sulphuric acid, the latter of which combines with undecomposed potassa. Those views were at the same time supported by Gay-Lussac. (An. de Ch. et Ph. vi.)

One of the chief arguments adduced by Vauquelin in support of his opinion was drawn from the action of charcoal on sulphate of potassa. When a mixture of this salt with powdered charcoal is ignited without exposure to the air, carbonic oxide and carbonic acid gases are formed, and a sulphuret is left, analogous both in appearance and properties to that which may be made by igniting carbonate of potassa directly with sulphur. They are both essentially the same substance, and Vauquelin conceived from the strong attraction of carbon for oxygen, that both the sulphuric acid and potassa would be decomposed by charcoal at a high temperature; and that, consequently, the product must be a sulphuret of potassium.

Berthier has proved that these changes do actually occur. (An. de Ch. et de Ph. xxii.) He put a known weight of sulphate of baryta into a crucible lined with a mixture of clay and charcoal, defended it from contact with the air, and exposed it to a white heat for the space of two hours. By this treatment it suffered complete decomposition, and it was found that in passing into a sulphuret, it had suffered a loss in weight precisely equal to the quantity of oxygen originally contained in the acid and earth. This circumstance, coupled with the fact that there had been no loss of sulphur, is decisive evidence that the baryta as well as the acid had lost its oxygen, and that a sulphuret of barium had been formed. He obtained the same results also with the sulphates of strontia, lime, potassa, and soda; but from the easy fusibility of the sulphurets of potassium and sodium, their loss of weight could not be determined with such precision as in the other instances.

The experiments of Berzelius, performed about the same time, are exceedingly elegant, and still more satisfactory than the foregoing. (An de Ch. et Ph. xx.) He transmitted a current of dry hydrogen gas over a known quantity of sulphate of potassa, heated to redness. It was expected from the strong affinity of hydrogen for oxygen, that the sulphate would be decomposed; and, accordingly, a considerable quantity of water was formed, which was carefully collected and weighed. The loss of weight which the salt had experienced was precisely equivalent to the oxygen of the acid and alkali; and the oxygen of the water was exactly equal to the loss in weight. A similar result was obtained with the sulphates of soda, baryta, strontia, and lime.

It is demonstrated, therefore, that the metallic bases of the alkalies and alkaline earths agree with the common metals in their disposition to unite with sulphur. It is now certain that, whether a sulphate be decomposed by hydrogen or charcoal, or sulphur ignited with an alkali or an alkaline earth, a metallic sulphuret is always the product. Direct combination between sulphur and a metallic oxide is a very rare occurrence, nor has the existence of such a compound been clearly established. Gay-Lussac indeed states that, when an alkali or an alkaline earth is heated with sulphur in such a manner that the temperature is never so high as a low red heat, the product is really the sulphuret of an oxide. But the facts adduced in favour of this opinion are not altogether satisfactory, so that the real nature of the product must be decided by future observation.

Several of the metallic sulphurets occur abundantly in nature. Those that are most frequently met with are the sulphurets of lead, antimony, copper, iron, zinc, molybdenum, and silver.

The metallic seleniurets have so close a resemblance in their chemical relations to the sulphurets, that it is unnecessary to give a separate description of them. They may be prepared either by bringing selenium in contact with the metals at a high temperature, or by the action of hydroselenic acid or metallic solutions.

Respecting the preceding compounds there remains one subject, the consideration of which, as applying equally to all, has been purposely delayed. The non-metallic ingredient of each is the radical of a hydracid, that is, has the property of forming with hydrogen an acid, which, like other acids, is unable to unite with metals, but appears to combine readily with many metallic oxides. Owing to this circumstance, a difficulty arises in explaining the action of such substances on water. Thus, when chloride of potassium is put into water, it may dissolve without suffering any other chemical change, and the liquid accordingly contain chloride of potassium in solution. But it is also possible that the elements of this compound may react on those of water, its potassium uniting with oxygen, and its chlorine with hydrogen; and as the resulting potassa and hydrochloric acid have a strong affinity for each other, the solution would of course contain hydrochlorate of potassa. A similar uncertainty attends the action of water on other metallic chlorides, and on the compounds of metals with iodine, bromine, sulphur, and similar substances; so that when iodide, sulphuret, and cyanuret of potassium are put into water, it may be doubted whether they dissolve as such, or whether they may not be converted, by decomposition of water, into hydriodate, hydrosulphate, and hydrocyanate of potassa. This question would at once be decided, could it be ascertained whether water is or is not decomposed during the process of solution; but this is the precise point of difficulty, since, from the operation of the laws of chemical union, no disengagement of gas does or can take place by which the occurrence of such a change may be indicated. Chemists, accordingly, being guided by probabilities, are divided in opinion, and I shall therefore give a brief statement of both views, with the arguments in favour of each.

According to one view, then, chloride of potassium and all similar compounds dissolve in water without undergoing any other change, and are deposited in their original state by crystallization. When any hydracid, such as hydrochloric or hydriodic acid, is mixed with potassa or any similar metallic oxide, the acid and salifiable base do not unite, but the oxygen of the oxide combines with the hydrogen of the acid, and the metal itself with the radical of the hydracid. This kind of double decomposition unquestionably takes place in some instances, as when hydrosulphuric acid acts upon acetate of oxide of lead, the insoluble sulphuret of lead being actually precipitated; but it is also thought to occur even when the transparency of the solution is undisturbed. It is argued, accordingly, that hydrochlorate of potassa, and the salts of the hydracids in general, have no existence. Thus, when nitrate of the oxide of silver is added to a solution of chloride of potassium, metallic silver is said to unite with chlorine, while the oxygen of the oxide of silver combines with potassium; so that nitrate of potassa and chloride of silver are generated. On adding sulphuric acid to a solution of chloride of potassium, hydrochloric acid and potassa, not previously existing, are instantly formed in consequence of the decomposition of water, which yields its hydrogen to chlorine, and its oxygen to potassium; exactly as happens when concentrated sulphuric acid is brought into contact with solid chloride of potassium. It is further believed that the crystallized hydrochlorate of lime, baryta, and strontia, which contain water or its elements, are metallic chlorides combined with water of crystallization; and the same view is applied to all analogous compounds.

According to the other doctrine, chloride of potassium is converted into hydrochlorate of potassa in the act of dissolving; and when the solution is evaporated, the elements existing in the salt reunite at the moment of crystallization, and crystals of chloride of potassium are deposited. The same explanation applies in all cases, when the salt of a hydracid crystallizes without retaining the elements of water. Of those compounds which in crystallizing retain water or its elements in combination, two opinions may be formed. Thus crystallized hydrochlorate of baryta, which consists of one equivalent of chlorine, one of barium, two of oxygen, and two of hydrogen, may be regarded as a compound either of hydrochlorate of baryta with one equivalent of water of crystallization, or of chloride of barium with two equivalents of water. When exposed to heat, two equivalents of water are expelled, and chloride of barium is left. When nitrate of the oxide of silver is mixed in solution with hydrochlorate of potassa, the oxygen of the oxide of silver unites with the hydrogen of the hydrochloric acid, chloride of silver is precipitated, and nitrate of potassa remains in the liquid. On adding sulphuric acid to a hydrochlorate, hydrochloric acid is simply displaced, just as when carbonic acid in marble is separated from lime by the action of nitric acid.

On comparing these opinions it is manifest that both are consistent with well-known affinities. When a metallic chloride is dissolved in water, the attraction of chlorine for the metal, and that of oxygen for hydrogen, tend to prevent chemical change; but the affinities of the metal for oxygen, of chlorine for hydrogen, and of hydrochloric acid for metallic oxides, co-operate in determining the decomposition of water, and the production of a hydrochlorate. In favour of the latter view, the following considerations may be adduced:—1. The solution of some compounds, such as sulphuret of potassium, actually emit an odour of hydrosulphuric acid. 2. Other compounds, such as the chlorides of copper, cobalt, and nickel, instantly acquire, when put into water, the colour peculiar to the salts of the oxides of those metals. 3. The solution of protochloride of iron, like the protosulphate, absorbs oxygen from the atmosphere; an effect which seems to indicate the presence of the protoxide of iron in the liquid. 4. In some instances there is direct proof of decomposition of water. Thus when sulphuret of aluminium is put into that fluid, alumina is generated, and hydrosulphuric acid gas disengaged with effervescence. In like manner chloride and sulphuret of silicon are converted by water into silica and hydrochloric and hydrosulphuric acid. In these cases the want of affinity between the new compounds causes their separation, and thus affords direct proof that water is decomposed. But the affinities which produce this change do not appear so likely to be effective, as those which are in operation when chloride of potassium is put into water; especially when it is considered that the attraction of chlorine for hydrogen, and potassium for oxygen, is aided by that of the resulting acid and oxide for each other.

These arguments may be successively answered in the following manner:—1. That solutions of cyanuret and sulphuret of potassium smell of hydrocyanic and hydrosulphuric acids, because the carbonic acid of the atmosphere gradually decomposes them. 2. That metals may yield with chlorine compounds of the same colour as the oxides of the same metals. Thus the terchloride and terfluoride of chromium have a red colour closely resembling that of chromic acid. 3. Protochloride of iron may attract oxygen from the air because of its known tendency to pass into the state of a sesquichloride, a portion of iron being at the same time converted into peroxide. 4. That while certain chlorides do really decompose water, it must be conceded that others dissolve directly without change. The bichloride of platinum and terchloride of gold are soluble in ether, forming solutions which must be regarded as chlorides and not hydrochlorates, since pure ether is anhydrous; and when aqueous solutions of these chlorides are agitated with ether, ethereal solutions of platinum and gold are formed, exactly similar to those made with ether alone. It can scarcely be doubted, then, that these chlorides exist as such in water. In favour of the same view it may with truth be alleged, that the chlorides of potassium and sodium dissolve in and crystallize out of water without evincing the least sign of any other change than mere solution and mere crystallization. Again, crystals of the so-called hydrochlorate of baryta become chloride of barium with loss of water by mere exposure to a dry air; a cause apparently inadequate to determine the hydrogen of the acid to unite with the oxygen of the oxide, but sufficient to explain the phenomena if the crystals were chloride of barium with water of crystallization.

On weighing these and other considerations of a like kind, it appears undeniable that *some* metallic chlorides, iodides, and similar compounds dissolve as such in water: that all do so, is a position which cannot, I think, be maintained; and therefore the existence of such compounds as hydracids united with metallic oxides, can scarcely be denied; and in the case of chloride of aluminium, which cannot be recovered from its solution in water, but yields alumina and hydrochloric acid, the change is obvious to the senses. At the same time it is necessary, to avoid a perpetually recurring two-fold explanation, to adhere consistently to one view; and the reader may have observed that I have, in this edition, uniformly gone on the supposition that chlorides, and the same class of bodies, dissolve as such in water. The considerations which have led to this preference are principally drawn from the history of the sulphur-salts.

Chemists are acquainted with several metallic phosphurets; and it is probable that phosphorus, like sulphur, is capable of uniting with all the metals. Little attention, however, has hitherto been devoted to their compounds; and for the greater part of our knowledge concerning them we are indebted to the researches of Pelletier and Rose. (An. de Ch. i. and xiii.; and Pog. An. vi. 205.)

The metallic phosphurets may be prepared in several ways. The most direct method is by bringing phosphorus in contact with metals at a high temperature, or by igniting metals in contact with phosphoric acid and charcoal. Several of the phosphurets may be formed by transmitting a current of phosphuretted hydrogen gas over metallic oxides heated to redness in a porcelain tube, when water is generated, and a phosphuret of the metal remains. By similar treatment the chlorides and sulphurets of many metals may be decomposed, and phosphurets formed, provided the metal is capable of retaining phosphorus at a red heat. According to Rose, the phosphurets of copper, nickel, cobalt, and iron are the only ones which admit of being advantageously prepared by this method. When chlorides are employed, hydrochloric acid, and with sulphurets hydrosulphuric acid gas, is of course generated.

Phosphorus is said to unite with metallic oxides. For example, phosphuret of lime is said to be formed by conducting the vapour of phosphorus over that earth at a low red heat; but it is probable that in this instance, as with a mixture of sulphur and an alkali, part of the metallic oxide is decomposed, and that the product contains phosphuret of calcium and phosphate of lime.

The only metallic carburets of importance are those of iron, which will be described in the section on that metal.

Hydrogen unites with few metals. The only metallic hydrogurets, or hydurets, known are those of zinc, potassium, arsenic, antimony, and tellurium. No definite compound of nitrogen and a metal has hitherto been discovered.

The discoveries of modern chemistry have materially added to the number of the metals, especially by associating with them a class of bodies which was formerly believed to be of a nature entirely different. The metallic bases of the alkalies and earths, previous to the year 1807, were altogether unknown; and before that date the list of metals, with few exceptions, included those only which are commonly employed in the arts and which are hence often called the common metals. In consequence of this increase in number, it is found convenient, for the purpose of description, to arrange them in separate groups; and as the alkalies and earths differ in several respects from the oxides of other metals, it will be convenient to describe them separately. I have accordingly divided the metals into the two following classes:—

Class I. Metals which by oxidation yield alkalies and earths.

Class II. Metals, the oxides of which are neither alkalies nor earths.

Class I. This class includes 12 metals, which may properly be arranged in three orders.

Order 1. Metallic bases of the alkalies. They are three in number; namely,

Potassium, Sodium, Lithium.

These metals have such a powerful attraction for oxygen, that they decompose cold water and even ice at the moment of contact, and are oxidized with disengagement of hydrogen gas. The resulting oxides are distinguished by their causticity and solubility in water, and by possessing alkaline properties in an eminent degree. They are called *alkalies*, and their metallic bases are sometimes termed *alkaline* or *alkaligenous* metals.

Order 2. Metallic bases of the alkaline earths. These are four in number; namely,

Barium, Strontium, Calcium, Magnesium.

These metals, excepting magnesium, also decompose water rapidly at common temperatures. The resulting oxides are called *alkaline earths;* because, while in their appearance they resemble the earths, they are similar to the alkalies in having a strong alkaline reaction with test paper, and in neutralizing acids. The three first are strongly caustic, and baryta and strontia are soluble in water to a considerable extent.

Order 3. Metallic bases of the earths. These are five in number; namely,

Aluminium, Glucinium, Yttrium.
Thorium, Zirconium,

The oxides of these metals are well known as the pure earths. They are white and of an earthy appearance, in their ordinary state are quite insoluble in water, and do not affect the colour of turmeric or litmus paper. As salifiable bases they are inferior to the alkaline earths.

Class II. The number of the metals included in this class amounts to 30. They are all capable of uniting with oxygen, and generally in more than one proportion. Their protoxides have an earthy appearance, but with few exceptions are coloured. They are insoluble in water, and in general do not affect the colour of test paper. Most of them act as salifiable bases in uniting with acids, and forming salts; but in this respect they are much inferior to the alkalies and alkaline earths, by which they may be separated from their combinations. Several of these metals are capable of forming with oxygen compounds, which possess the characters of acids. The metals in which this property has been noticed are, manganese, arsenic, chromium, vanadium, molybdenum, tungsten, antimony, columbium, titanium, tellurium, gold, and osmium.

The metals belonging to the second class may be conveniently arranged in the three following orders:—

Order 1. Metals which decompose water at a red heat. They are seven in number; namely,

Manganese,
Zinc,
Iron,
Tin,
Cadmium,
Cobalt,
Nickel.

Order 2. Metals which do not decompose water at any temperature, and the oxides of which are not reduced to the metallic state by the sole action of heat. Of these there are fifteen in number; namely,

Arsenic,
Chromium,
Vanadium,
Molybdenum,
Tungsten,
Columbium,
Antimony,
Uranium,
Cerium,
Lantanium,
Bismuth,
Titanium,
Tellurium,
Copper,
Lead.

Order 3. Metals, the oxides of which are decomposed by a red heat. These are,

Mercury,
Silver,
Gold,
Platinum,
Palladium,
Rhodium,
Osmium,
Iridium.

CLASS I.

METALS WHICH BY OXIDATION YIELD ALKALIES OR EARTHS.

ORDER I.

METALLIC BASES OF THE ALKALIES.

SECTION I.

POTASSIUM.

Hist. and Prep.—Discovered in the year 1807 by Davy, and the circumstances which led to the discovery have already been described. Hydrate of potassa, slightly moistened for the purpose of increasing its conducting power, was made to communicate with the opposite poles of a galvanic battery of 200 double plates; when the oxygen both of the water and the potassa passed over to the positive pole, while the hydrogen of the former, and the potassium of the latter, made their appearance at the negative pole. By this process potassium is obtained in small quantity only; but Gay-Lussac and Thenard invented a method by which a more abundant supply may be procured. (Recherches Physico-Chimiques, vol. i.) Their process consists in bringing fused hydrate of potassa in contact with turnings of iron heated to whiteness in a gun-barrel. The iron, under these circumstances, deprives the water and potassa of oxygen, hydrogen gas combined with a little potassium is evolved, and pure potassium sublimes, and may be collected in a cool part of the apparatus.

Potassium may also be prepared, as first noticed by Curaudau, by mixing dry carbonate of potassa with half its weight of powdered charcoal, and exposing the mixture, contained in a gun-barrel or spheroidal iron bottle, to a strong heat. An improvement on both processes has been made by Brunner, who decomposes potassa by means of iron and charcoal. From eight ounces of fused carbonate of potassa, six ounces of iron filings, and two ounces of charcoal, mixed intimately and heated in an iron bottle, he obtained 140 grains of potassium. (Quarterly Journal, xv. 379.) Berzelius has observed that the potassium thus made, though fit for all the usual purposes to which it is applied, contains a minute quantity of carbon; and therefore, if required to be quite pure, must be rendered so by distillation in a retort of iron or green glass. A modification of this process has been since described by Wöhler, who effects the decomposition of the potassa solely by means of charcoal. The material employed for the purpose is carbonate of potassa prepared by heating cream of tartar to redness in a covered crucible. (Poggendorff's Annalen, iv. 23.) According to Liebig, 2 eq. of charcoal and 1 eq. of carbonate of potassa react on each other, and form 1 eq. of potassium and 3 eq. of carbonic oxide; or

$$\begin{matrix} KO + CO_2 \\ \text{and } 2C \end{matrix} \;\text{yield}\; \begin{matrix} K \\ \text{and } 3CO. \end{matrix}$$

The whole of the potassium thus liberated is not, however, obtained in the metallic form, for 2 out of every 3 eq. combine with 7 out of the 9 eq. of carbonic oxide gas at the same time produced. The resulting compound has a dark grey colour, and is recognised by burning on water with a violent flame, and the production of croconate and oxalate of potassa. This compound is sometimes almost the sole product of the process. (Geiger's Pharmacie, 348.)

Prop.—Solid at the ordinary temperature of the atmosphere. At 70° it is somewhat fluid, though its fluidity is not perfect till it is heated to 150°. At 50° it is soft and malleable, and yields like wax to the pressure of the fingers; but it becomes brittle when cooled to 32°. It sublimes at a low red heat without undergoing any change, provided atmospheric air be completely excluded. Its texture is crystalline, as may be seen by breaking it across while brittle, and cubic crystals have been obtained by Pleischl (Pog. An. xxxi. 431). In colour and lustre it is precisely similar to mercury. At 60° its density is 0·865, so that it is considerably lighter than water. It is quite opaque, and is a good conductor of heat and electricity.

The most prominent chemical property of potassium is its affinity for oxygen gas. It oxidizes rapidly in the air, or by contact with fluids which contain oxygen. On this account it must be preserved either in glass tubes hermetically sealed, or under the surface of liquids, such as naphtha, of which oxygen is not an element. If heated in the open air, it takes fire, and burns with a purple flame and great evolution of heat. It decomposes water on the instant of touching it; and so much heat is disengaged, that the potassium is inflamed, and burns vividly while swimming upon its surface.

The hydrogen unites with a little potassium at the moment of separation; and this compound takes fire as it escapes, and thus augments the brilliancy of the combustion. When potassium is plunged under water, violent reaction ensues, but without light, and pure hydrogen gas is evolved.

The combining weight or equivalent of potassium is easily deducible from the composition of potassa and chloride of potassium, which are admitted to consist of single equivalents of their elements. Gay-Lussac and Thenard, and Davy, inferred the composition of potassa from the hydrogen gas evolved when a known weight of potassium is oxidized under water, the volume of the oxygen which unites with the metal being equal to half the volume of the hydrogen. Berzelius analyzed chloride of potassium by means of nitrate of oxide of silver, and inferred that 39·15 is the eq. of potassium. Its symb. is K.

	Potassium.			Equiv.		Formulæ.
Protoxide	39·15	1 eq.+Oxygen	8	1 eq. =	47·15	$K+O$ or KO.
Peroxide	39·15	1 eq.+ . .	24	3 eq. =	63·15	$K+3O$ or KO_3.
Chloride	39·15	1 eq.+Chlor.	35·42	1 eq. =	74·57	$K+Cl$ or KCl.
Iodide	39·15	1 eq.+Iodine	126·3	1 eq. =	165·45	$K+I$ or KI.
Bromide	39·15	1 eq.+Brom.	78·4	1 eq. =	117·55	$K+Br.$ or KBr.
Fluoride	39·15	1 eq.+Fluor.	18·68	1 eq. =	57·83	$K+F$ or KF.
Hydurets Carburet	Composition uncertain.					
Sulphuret	39·15	1 eq.+Sulphur	16·1	1 eq. =	55·25	$K+S$ or KS.
Bisulphuret	39·15	1 eq.+do.	32·2	2 eq. =	71·35	$K+2S$ or KS_2.
Tersulphuret	39·15	1 eq.+do.	48·3	3 eq. =	87·45	$K+3S$ or KS_3.
Quadrosulphuret	39·15	1 eq.+do.	64·4	4 eq. =	103·35	$K+4S$ or KS_4.
Quintosulphuret	39·15	1 eq.+do.	80·5	5 eq. =	119·65	$K+5S$ or KS_5.
Phosphurets Seleniurets	Composition and number uncertain.					

Protoxide of Potassium.—Hist. and Prep.—This compound, commonly called *potash* or *potassa*, and by the Germans *kali* (an Arabic word), is always formed when potassium is put into water, or when it is exposed at common temperatures to dry air or oxygen gas. By the former method the protoxide is obtained in combination with water; and in the latter it is anhydrous. In performing the last-mentioned process, the potassium should be cut into very thin slices; for otherwise the oxidation is incomplete. The product, when partially oxidized, is regarded by Berzelius as a distinct oxide; but most chemists admit it to be a mere mixture of potassa and potassium.

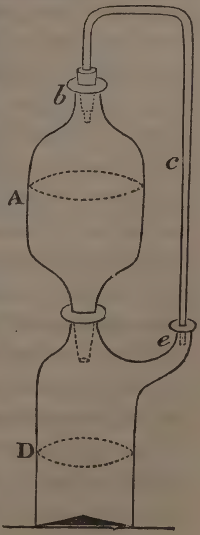
Prop.—Anhydrous potassa is a white solid substance, highly caustic, which fuses at a temperature somewhat above that of redness, and bears the strongest heat of a wind furnace without being decomposed or volatilized. It has a powerful affinity for water, and intense heat is disengaged during the act of combination. Three compounds are known; they are composed of 47·15, or 1 eq. of potassa united with 9, 27, and 45 parts, or 1, 3, and 5 eq. of water respectively. In the last compound a portion of the water probably exists as water of crystallization.

The protohydrate of potassa is solid at common temperatures. It fuses at a heat rather below redness, and assumes a somewhat crystalline texture in cooling. It is not decomposed by any degree of heat to which it has been exposed, and hence was long considered to be pure potassa. Its sp. gr. = 1·706. It is highly deliquescent, and requires about half its weight of water for solution. It is soluble, likewise, in alcohol. It destroys all animal textures, and on this account is employed in surgery as a caustic. It was formerly called *lapis causticus*, but it is now termed *potassa* and *potassa fusa* by the Colleges of Edinburgh and London. This preparation is made by evaporating the aqueous solution of potassa in a silver or clean iron capsule to the consistence of oil, and then pouring it into moulds. In this state it is impure, containing oxide of iron, together with chloride of potassium, and carbonate and sulphate of potassa. It is purified from these substances by solution in alcohol, and evaporation to the same extent as before in a silver vessel. The operation should be performed expeditiously, in order to prevent, as far as possible, the absorption of carbonic acid. When common caustic potassa of the druggists is dissolved in water, a number of small bubbles of gas is disengaged, which is pure oxygen. Graham finds its quantity to be variable in different specimens, and to depend apparently on the impurity of the specimen.

If the protohydrate be exposed to the air, it rapidly becomes moist; but after absorbing a certain portion of water, a perfectly dry substance is again obtained, which is the terhydrate of potassa. It is very similar in all its characters to the protohydrate, but is much whiter and more crystalline in its texture. The quintohydrate is obtained by exposing a very concentrated solution of potassa to an intense cold. It is then deposited in four-sided prisms terminated by a four-sided pyramid, and sometimes in four-sided tables and octohedrons.

The aqueous solution of potassa, *aqua potassæ* of the Pharmacopœia, is prepared by decomposing carbonate of potassa by lime. The best proportions are 1 part of dry lime to 2 of carbonate of potassa. The lime is to be slaked by being covered with boiling water, when it forms a very minutely divided hydrate, in the form of a cream, every particle of which acts, which is not the case in dry slaking (Mohr). The carbonate is now dissolved in not less than 10 parts of hot water, and the cream of lime is added by small portions to the solution, and the mixture boiled after each addition in a clean iron vessel. The lime takes the carbonic acid, forming insoluble carbonate of lime. When the whole lime has been added, and the mixture has been boiled for some time, it is allowed to subside in the covered vessel, and the solution of caustic potassa may be decanted perfectly clear. If the carbonate have been pure, the solution yields by rapid evaporation pure hydrate of potassa. But if pearlash be employed, the sulphate of potash contained in it may be got rid of by evaporating till crystals appear; on cooling, the sulphate is so completely deposited that its presence can no longer be detected in the liquid (Liebig). The same chemist finds that a strong solution of caustic potassa actually deprives carbonate of lime of its acid, and that, from this circumstance, carbonate of potassa cannot be rendered quite caustic by lime unless diluted with about ten times its weight of water.

As pure potassa absorbs carbonic acid rapidly when freely exposed to the atmosphere, it is desirable to filter its solution in vessels containing as small a quantity of air as possible. This is easily effected by means of the filtering apparatus devised by Donovan. It consists of two vessels A and D, of equal capacity, and connected with each other as represented in the annexed wood-cut. The neck *b* of the upper vessel contains a tight cork, perforated to admit one end of the glass tube *c*; and the lower extremity of the same vessel terminates in a funnel pipe, which fits into one of the necks of the under vessel D by grinding, luting, or a tight cork. The vessel D is furnished with another neck *e*, which receives the lower end of the tube *c*, the junction being secured by means of a perforated cork, or luting. The throat of the funnel pipe is obstructed by a piece of coarse linen loosely rolled up, and not pressed down into the pipe itself. The solution is then poured in through the mouth at *b*, the cork and tube having been removed; and the first droppings, which are turbid, are not received in the lower vessel. The parts of the apparatus are next joined together,



and the filtration may proceed at the slowest rate, without exposure to more air than was contained in the vessels at the beginning of the process. This apparatus should be made of green in preference to white glass, as the pure alkalies act on the former much less than on the latter. (Annals of Philosophy, xxvi. 115.)

The mode by which this apparatus acts scarcely needs explanation. In order that the liquid should descend freely, two conditions are required:—first, that the air above the liquid should have the same elastic force, and therefore exert the same pressure, as that below; and secondly, as one means of securing the first condition, that the air should have free egress from the lower vessel. Both objects, it is manifest, are accomplished in the filtering apparatus of Donovan; since for every drop of liquid which descends from the upper to the lower vessel, a corresponding portion of air passes along the tube *c* from the lower vessel to the upper. This apparatus is applicable to any other case where it is wished to exclude the atmosphere. Other similar contrivances will be found in the scientific journals, for which there is no space in this work.

Solution of potassa is highly caustic, and its taste intensely acrid. It possesses alkaline properties in an eminent degree, converting the vegetable blue colours to green, and neutralizing the strongest acids. It absorbs carbonic acid gas rapidly, and is consequently employed for withdrawing that substance from gaseous mixtures. When of the sp. gr. 1·25, it is used in the analysis of organic bodies, to absorb the carbonic acid formed, the weight of which is equal to the increase in the weight of the potash apparatus. The solution made from pearlash, which has deposited the sulphate of potash, is exactly of the proper strength for this purpose (Gregory). For the same reason it should be preserved in well-closed bottles, that it may not absorb carbonic acid from the atmosphere.

Potassa is employed as a reagent in detecting the presence of bodies, and in separating them from each other. The solid hydrate, owing to its strong affinity for water, is used for depriving gases of hygrometric moisture, and is admirably fitted for forming frigorific mixtures (page 42).

Potassa may be distinguished from all other substances by the following characters:—1. If tartaric acid be added in excess to a salt of potassa dissolved in cold water, and the solution be stirred with a glass rod, a white precipitate, bitartrate of potassa, soon appears, which forms peculiar white streaks upon the glass by the pressure of the rod in stirring. 2. It is precipitated by perchloric acid in the cold, the perchlorate of potassa having nearly the same degree of solubility as the bitartrate. 3. A solution of chloride of platinum causes a yellow precipitate, the double chloride of platinum and potassium. A drop or two of hydrochloric acid should be added at the same time as the test, the mixture be evaporated to dryness at 212°, and a little cold water be afterwards added, when the double chloride is left in the form of small shining yellow crystals. Chloride of platinum dissolved in alcohol often gives an immediate precipitate, which falls of a pale yellow colour. 4. The alcoholic solution of carbazotic acid throws down potassa in yellow crystals of carbazotate of potassa, which is very sparingly soluble. 5. It yields a light gelatinous precipitate, the double fluoride of potassium and silicon with silicated hydrofluoric acid. Of these tests carbazotic acid is the most delicate in a solution of pure potassa; but when the alkali is combined with a strong acid, the chloride of platinum is preferable.

The following test has been recommended by Harkort for distinguishing between potassa and soda in minerals:—Oxide of nickel, when fused by the blowpipe flame with borax, gives a brown glass; and this glass, if melted with a mineral containing potassa, becomes blue, an effect which is not produced by the presence of soda.

Its eq. is 47·15; symb. $K + O$, $\dot{K}$, or KO.

Peroxide.—When potassium burns in the open air or in oxygen gas, it is converted into an orange-coloured substance, which is peroxide of potassium. It may likewise be formed by conducting oxygen gas over potash at a red heat; and it is produced in small quantity when potash is heated in the open air. It is the residue of the decomposition of nitre by heat in metallic vessels, provided the temperature be kept up for a sufficient time. When the peroxide is put into water, it is resolved into oxygen and potash, the former of which escapes with effervescence, and the latter is dissolved. Its eq. is 63 15; symb. $K + 3O$, $\dddot{K}$, or KO_3.

Chloride of Potassium.—Potassium takes fire spontaneously in an atmosphere of chlorine, and burns with greater brilliancy than in oxygen gas. This chloride is generated with evolution of hydrogen when potassium is heated in hydrochloric acid gas; and it is the residue after the decomposition of chlorate of potassa by heat. It is formed when potassa is dissolved in a solution of hydrochloric acid, and is deposited by slow evaporation in anhydrous colourless cubic crystals. It has a saline and rather bitter taste, is insoluble in alcohol, and requires for solution 3 parts of water at 60°, and still less of hot water. Its eq. is 74·57; symb. K + Cl. or KCl.

Iodide of Potassium.—Prep.—This compound is formed with evolution of heat and light, when potassium is heated in contact with iodine; it is the sole residue after decomposing iodate of potassa by heat; and by neutralizing potassa with hydriodic acid it is obtained in solution. The simplest process for preparing it in quantity is to add iodine to a hot solution of pure potassa until the alkali is neutralized, when iodide of potassium and iodate of potassa are generated, evaporate to dryness, and expose the dry mass in a platinum crucible to a gentle red heat in order to decompose the iodate. The fused mass is then dissolved out by water and crystallized. (Gregory, Edin. Med. and Surg. Jour. 1830.) Another process is to digest iodine with zinc or iron filings in water, and then decompose the resulting iodide of zinc or iron by a quantity of potassa just sufficient to precipitate the oxide.

Prop.—Iodide of potassium fuses readily when heated, and rises in vapour at a heat below full redness, especially in an open vessel. It is very soluble in water, requiring only two-thirds of its weight at 60° for solution, and in a moist atmosphere deliquesces. It dissolves also in strong alcohol, even in the cold; and the solution, when evaporated, yields colourless cubic crystals of iodide of potassium.

The commercial iodide is frequently impure, often containing chloride of potassium or sodium, and sulphate or carbonate of potassa, the last sometimes in very large quantity. It is well to purchase it in crystals, which ought not to deliquesce in a moderately dry air, but when in powder are completely soluble in the strongest alcohol.

Iodine is freely soluble in water which contains iodide of potassium, a brown solution resulting, which has been thought to arise from potassium uniting with two or more equivalents of iodine. No solid compound of the kind, however, has been obtained.

Its eq. is 165·45; symb. K + I, or KI.

Bromide of Potassium.—This compound is formed by processes similar to those for preparing the iodide, and is analogous to it in most of its properties. It is very soluble in water, and crystallizes by evaporation in anhydrous cubic crystals, which fuse readily, and decrepitate when heated like sea-salt. It is but slightly soluble in alcohol. Its eq. is 117·55; symb. K + Br, or KBr.

Fluoride of Potassium.—This compound is best formed by nearly saturating hydrofluoric acid with carbonate of potassa, evaporating to dryness in platinum, and igniting to expel any excess of acid. The resulting fluoride has a sharp saline taste, is alkaline to test paper, deliquesces in the air, and dissolves freely in water. On evaporating its solution at a temperature of 100° it may be obtained in cubes or rectangular four-sided prisms, which deliquesce rapidly. The solution acts on glass in which it is kept or evaporated. Heated with silicic acid it forms a fusible limpid glass, which when cold is opaque and deliquescent. Water dissolves fluoride of potassium, and the silicic acid is left.

Its eq. is 57·83; symb. $K + F$, or KF.

Hydrogen and Potassium.—These substances unite in two proportions, forming in one case a solid, and in the other a gaseous compound. The latter is produced when hydrate of potash is decomposed by iron at a white heat, and it appears also to be generated when potassium burns on the surface of water. It inflames spontaneously in air or oxygen gas; but on standing for some hours over mercury, the greater part, if not the whole of the potassium, is deposited.

The solid hyduret of potassium was made by Gay-Lussac and Thenard, by heating potassium in hydrogen gas. It is a grey, solid substance, which is readily decomposed by heat or contact with water. It does not inflame spontaneously in oxygen gas.

Carburet of Potassium.—This compound has not been obtained in a pure state; but it is thought to form part of the residue in the preparation of potassium from charcoal; for on pouring that matter into water, effervescence ensues owing to the escape of carburetted hydrogen gas, and carbonate of potassa is found in solution.

Sulphurets of Potassium.—Potassium unites readily with sulphur by the aid of gentle heat, emitting so much heat that the mass becomes incandescent. The nature of the product depends on the proportions which are employed. The protosulphuret is readily prepared by decomposing sulphate of potassa by charcoal or hydrogen gas at a red heat. It may be prepared in the moist way by a process which will be mentioned in describing the sulphur-salts.

The protosulphuret of potassium fuses below a red heat, and acquires on cooling a crystalline texture. It has a red colour, its taste is at first strongly alkaline and then sulphurous, has an alkaline reaction with test paper, deliquesces on exposure to the air, and is soluble in water and alcohol. Most of the acids decompose it with evolution of hydrosulphuric acid gas, and without any deposite of sulphur. It takes fire when heated before the blowpipe, and quickly acquires a coating of sulphate of potassa, which stops the combustion; but when mixed in fine division with charcoal, it kindles spontaneously, forming a good pyrophorus.

It eq. is 55·25; symb. $K + S$, or KS.

The *bisulphuret* is formed by exposing a saturated solution in alcohol of hydrosulphate of sulphuret of potassium ($KS + HS$), until a pellicle begins to form upon its surface, and then evaporating to dryness without further exposure. The first change consists in oxygen of the air uniting with hydrogen of hydrosulphuric acid, the sulphur of which unites with potassium. Then the formation of hyposulphurous acid begins; and as the hyposulphite of potassa is insoluble in alcohol, it gives a pellicle on its surface. It may also be obtained from an aqueous solution of the protosulphuret. This compound, when pure, dissolves in water without colour; but exposed to the air, oxygen is rapidly absorbed, and the solution becomes yellow. The change is effected by one half of the potassium combining with oxygen and yielding its sulphur to the remainder by which the bisulphuret of potassium and potassa are formed. Thus $2KS$ yield KS_2, and KO. If the solution continues to be exposed, it again becomes colourless, owing to the conversion of the bisulphuret into hyposulphite of potassa.

Its eq. is 71·35; symb. $K + 2S$, or KS_2.

The *tersulphuret* is prepared pure by transmitting the vapour of bisulphuret of carbon over carbonate of potassa at a red heat, as long as carbonic acid or carbonic oxide gases are disengaged. It is also formed when carbonate of potassa is heated to low redness with half its weight of sulphur, until the mass appears in tranquil fusion: the oxygen of 3-4ths of the potassa unites with sulphur to form sulphuric acid, which exactly suffices to neutralize 1-4th of the alkali, and all the carbonic acid is evolved as gas.—Thus

4 eq. Potassa and 10 eq. Sulphur yield 3 eq. Tersulphuret and 1 eq. Sulphate.
$4KO$ S_{10} $3KS_3$ KO, SO_3.

This is known under the name of *liver of sulphur* (p. 362).

Its eq. is 87·45; symb. $K + 3S$, or KS_3.

The *quadrosulphuret* is prepared by transmitting the vapour of bisulphuret of carbon over sulphate of potassa at a red heat until carbonic acid gas ceases to be disengaged; or by conducting the same process with the tersulphuret prepared by the second method, until its sulphuric acid and potassa are decomposed.

Its eq. is 103·55; symb. $K + 4S$, or KS_4.

The *quintosulphuret* is formed by fusing carbonate of potassa with its own weight of sulphur, the residue containing sulphate of potassa as in preparing the tersulphuret. Each equivalent of potassium with five of sulphur, being the highest degree of sulphuration which can be formed by fusion.

Its eq. is 119·65; symb. $K + 5S$, or KS_5.

These four last sulphurets are deliquescent in the air, have a sulphurous odour, and are soluble in water; and those who consider them to decompose water in dissolving, suppose the formation of corresponding compounds of hydrogen and sulphur. On decomposing the solutions with hydrochloric or sulphuric acid, the changes ensue which have already been explained (page 336). As the solution of the quintosulphuret dissolves sulphur, a still higher degree of sulphuration must probably exist.

Two other compounds of sulphur and potassium, the composition of which are K_2S_7, and K_2S_9, have been described. The first of these is produced when sulphate of potassa is heated in a stream of sulphuretted hydrogen; and the latter, when the quadrosulphuret of potassium is heated in a similar manner. The definite nature of these compounds may be considered doubtful.

Phosphurets of Potassium.—When potassium is heated in phosphuretted hydrogen gas, it takes fire, phosphuret of potassium is formed, and hydrogen set free; and combination is also effected by gently heating phosphorus with potassium. The number and proportion of these compounds have not yet been determined. They decompose water with formation of phosphuretted hydrogen, potassa, and some acid of phosphorus.

Seleniurets of Potassium.—These elements unite when fused together, sometimes with explosive violence, forming a crystalline fusible compound of an iron grey colour and metallic lustre. It dissolves completely in water, yielding a deep red solution, very similar in taste and odour to solutions of sulphuret of potassium. On adding an acid, hydroselenic acid gas is evolved, and selenium deposited. Solution of potassa dissolves selenium, and gives rise to a seleniuret of potassium and selenite of potassa; and the same compounds are formed when selenium is heated with carbonate of potassa.

SECTION II.

SODIUM.

Hist. and Prep.—The *Natrium* of the Germans, was discovered in 1807, a few days after the discovery of potassium. The first portions of it were obtained by means of galvanism; but it may be procured in much larger quantity by chemical processes, precisely similar to those described in the last section. As sodium may be obtained in much larger quantity than potassium, owing to the fact that it does not combine, like the former, with carbonic acid, the method of preparing sodium as described by Schœdler (Liebig's Annalen, vol. xx. p. 2) is here briefly noticed. Three pounds of commercial acetate of soda are ignited, and the residue, which weighs 1 lb. consisting of carbonate mixed with charcoal, is further mixed with $\frac{1}{4}$ lb. of finely-powdered charcoal and $\frac{1}{2}$ lb. of charcoal in coarser particles, to prevent fusion of the mass. It is then heated in the usual manner in an iron bottle, such as is used for holding mercury in commerce. This process is so productive that in one operation with the above quantities Schœdler obtained 4$\frac{1}{2}$ oz. of pure sodium. As a quantity half larger may be heated in such a bottle, it is possible to obtain in one operation upwards of 6 oz. of sodium; and this from the cheapest materials. Sodium thus prepared has been sold at three or four shillings per ounce. It might be made much cheaper even than this, and as it oxidizes less rapidly than potassium, it is much better adapted for experiments of research.

Prop.—It has a strong metallic lustre, and in colour is very analogous to silver. It is so soft at common temperatures, that it may be formed into leaves by the pressure of the fingers. It fuses at 200°, and rises in vapour at a red heat. Its sp. gr. is 0·972. It soon tarnishes on exposure to the air, though less rapidly than potassium. Like that metal, it is instantly oxidized by water, hydrogen gas in temporary union with a little sodium being disengaged. When thrown on cold water, it swims on its surface, and is rapidly oxidized, though in general without inflaming; but with hot water it scintillates, or even takes fire. Ducatel finds that the heat rises high enough for inflammation with cold water, if the sodium be confined to one spot, and the water rest on a non-conducting substance, such as charcoal. (Silliman's Journal, xxv. 90.) In each case, soda is generated, and the water acquires an alkaline reaction.

The composition of soda was determined by the same methods as that of potassa, and agreeably to the observations of Berzelius 23·3 may be taken as the eq. of sodium. Its symb. is Na. The composition of the compounds of sodium described in this section is as follows :—

	Sodium.			Equiv.	Formulæ.
Protoxide	. 23·3	1 eq.+Oxygen	8	1 eq.= 31·3	Na+O or $\dot{\mathrm{Na}}$.
Peroxide	. 46·6	2 eq.+do.	24	3 eq.= 70·6	2Na+3O or $\underline{\dddot{\mathrm{Na}}}$.
Chloride .	. 23·3	1 eq.+Chlorine	35·42	1 eq.= 58·72	Na+Cl or Na Cl.
Iodide .	. 23·3	1 eq.+Iodine	126·3	1 eq.=149·6	Na+I or Na I.
Bromide .	. 23·3	1 eq.+Bromine	78·4	1 eq.=101·7	Na+Br.or NaBr.
Fluoride .	. 23·3	1 eq.+Fluorine	18·68	1 eq.= 41·98	Na+F or Na F.
Sulphuret	. 23·3	1 eq.+Sulphur	16·1	1 eq.= 39·4	Na+S or Na S.

Soda.— Prep.— The protoxide of sodium, commonly called *soda*, and by the Germans *natron*, is formed by the oxidation of sodium in air or water, as potassa is from potassium. In its anhydrous state it is a grey solid, difficult of fusion, and very similar in all its characters to potassa. With water it forms a solid hydrate, easily fusible by heat, which is very caustic, soluble in water and alcohol, has powerful alkaline properties, and in all its chemical relations is exceedingly analogous to potassa. It is prepared from the solution of pure soda, exactly in the same manner as the corresponding preparations of potassa. The solid hydrate is composed of 31·3 parts or 1 eq. of soda, and 9 parts or 1 eq. of water.

Prop.—Soda is readily distinguished from other alkaline bases by the following characters. 1. It yields, with sulphuric acid, a salt which, by its taste and form, is easily recognized as Glauber's salt, or sulphate of soda. 2. All its salts are soluble in water, and are not precipitated by any reagent. 3. On exposing its salts by means of platinum wire to the blowpipe flame, they communicate to it a rich yellow colour.

Its eq. is 31·3 ; symb. $\mathrm{Na} + \mathrm{O}$, $\dot{\mathrm{Na}}$, or NaO.

Peroxide of Sodium.—This compound is formed when sodium is heated to redness in an excess of oxygen gas. It has an orange colour, has neither acid nor alkaline properties, and is resolved by water into soda and oxygen.

Its eq. is 70·6 ; symb. $2\mathrm{Na} + 3\mathrm{O}$, $\underline{\dddot{\mathrm{Na}}}$, or $\mathrm{Na_2O_3}$.

Chloride of Sodium.—Hist. and Prep.—This compound may be formed directly by burning sodium in chlorine, by heating sodium in hydrochloric acid gas, and by neutralizing soda with hydrochloric acid. It exists as a mineral under the name of *rock salt*, is the chief ingredient of sea-water, and is contained in many saline springs. From these sources are derived the different varieties of common salt, such as rock, bay, fishery, and stoved salt, which differ from each other only in degrees of purity and mode of preparation. The rock and bay salt are the purest, but always contain small quantities of sulphate of magnesia and lime, and chloride of magnesium. These earths may be precipitated as carbonates by boiling a solution of salt for a few minutes with a slight excess of carbonate of soda, filtering the liquid, and neutralizing with hydrochloric acid. On evaporating this solution rapidly, chloride of sodium crystallizes in hollow four-sided pyramids; but it occurs in regular cubic crystals when the solution is allowed to evaporate spontaneously. These crystals contain no water of crystallization, but decrepitate remarkably when heated, owing to the expansion of water mechanically confined within them.

Prop.—Pure chloride of sodium has an agreeably saline taste. It fuses at a red heat, and becomes a transparent brittle mass on cooling. It deliquesces slightly in a moist atmosphere, but undergoes no change when the air is dry. In pure alcohol it is insoluble. It requires twice and a half its weight of water at 60° for solution, and its solubility is not increased by heat. Hydrous sulphuric acid decomposes it with evolution of hydrochloric acid gas, and formation of sulphate of soda.

The uses of chloride of sodium are well known. Besides its employment in seasoning food, and in preserving meat from putrefaction, a property which, when pure, it possesses in a high degree, it is used for various purposes in the arts, especially in the formation of hydrochloric acid and hypochlorite of lime.

Its eq. is 58·72; symb. $Na + Cl$, or $NaCl$.

Iodide of Sodium.—It is obtained pure by processes similar to those for preparing iodide of potassium; but it is contained in sea-water, in many salt springs, and in the residual liquor from kelp. It is a neutral compound, deliquescent in the air, soluble in water and alcohol, fuses readily by heat, and is volatile, though in a less degree than iodide of potassium. Evaporated at 123° it crystallizes from its aqueous solution in cubes, which Berzelius found to contain 20·23 per cent. of water.

Its eq. is 149·6; symb. $Na + I$, or NaI.

Bromide of Sodium.—This compound is very analogous to sea-salt, and is associated with it in sea-water and most salt springs. At 86° it crystallizes from its aqueous solution in anhydrous cubes; but at lower temperatures it separates in hexagonal tables, which Mitscherlich found to contain 26·37 per cent. of water, or 4 eq. to 1 eq. of the bromide.

Its eq. is 101·7; symb. $Na + Br$, or $NaBr$.

Fluoride of Sodium.—This compound is formed by neutralizing hydrofluoric acid by soda, and by igniting the double fluoride of sodium and silicon, when the fluoride of silicon is expelled. When obtained by the second process, it crystallizes from its aqueous solution in rhomboidal crystals, but is obtained in cubes, its proper form, by a second crystallization: when carbonate of soda is present, it crystallizes in octohedrons.

Fluoride of sodium in crystals is anhydrous, is almost insoluble in alcohol, and requires 25 times its weight both of hot and cold water for solution. It attacks glass vessels when evaporated in them, and by fusion unites with silicic acid, forming a glass which is more fusible than the pure fluoride; but water dissolves out the fluoride, and leaves the silicic acid.

Its eq. is 41·98; symb. $Na + F$, or NaF.

Sulphuret of Sodium.—The protosulphuret is obtained by processes similar to those for protosulphuret of potassium, to which in its taste and chemical relations it is very similar. A concentrated solution of it yields hydrated, square, four-sided prisms, which, when heated, fuse in their water of crystallization, and then leave a white anhydrous mass. It deliquesces in the air, is very soluble in water, and is also dissolved, though in a smaller degree, by alcohol. In solution it absorbs oxygen very rapidly from the air, and passes into hyposulphate of soda.

Its eq. is 39·4; symb. $Na + S$, or NaS.

Sodium unites with sulphur in other proportions; but the resulting compounds have not been studied.

According to Gmelin of Tübingen, sulphuret of sodium is the colouring principle of *lapis lazuli*, to which the colour of ultramarine is owing; and he has succeeded in preparing artificial ultramarine by heating sulphuret of sodium with a mixture of silicic acid and alumina. (An. de Ch. et Ph. xxxvii. 409.) Artificial ultramarine, thus prepared, is sold in Paris at a moderate price. The finer specimens are quite equal to the native ultramarine, and much less expensive.

SECTION III.

LITHIUM.

Davy succeeded by means of galvanism in obtaining from lithia a white-coloured metal like sodium; but it was oxidized, and thus reconverted into lithia, with such rapidity that its properties could not be farther examined. Its eq. inferred from the composition of sulphate of lithia by Stromeyer and Thomson, is 10; but the accuracy of this estimate is rendered doubtful by the experiments of M. Herrman, according to which 6 is a nearer estimate. Its symb. is L. The compounds of lithium described in this section are thus constituted:—

	Lithium.			Equiv.	Formulæ.
Lithia	6	1 eq.+Oxygen	8	1 eq.=14	$L+O$ or LO.
Chloride	6	1 eq.+Chlorine	35·42	1 eq.=41·42	$L+Cl$ or LCl.
Fluoride	6	1 eq.+Fluorine	18·68	1 eq =24·68	$L+F$ or LF.

Lithia.—Hist.—This, the only known oxide of lithium, was discovered in 1818 by M. Arfwedson (An. de Ch. et Ph. x.) in a mineral called *petalite;* and its presence has since been detected in spodumene, lepidolite, and in several varieties of mica. Berzelius has found it also in the waters of Carlsbad in Bohemia. From the circumstance of its having been first obtained from an earthy mineral Arfwedson gave it the name of *lithion*, (from λιθειος, *lapideus*,) a term since changed in this country to *lithia*. It has hitherto been procured in small quantity only, because spodumene and petalite are rare, and do not contain more than 6 or 8 per cent. of the alkali. It is combined in these two minerals with silicic acid and alumina, whereas potassa is likewise present in lepidolite and lithion-mica, and therefore lithia should be prepared solely from the former.

Prep.—The best process for preparing lithia is that which was suggested by Berzelius. One part of petalite or spodumene, in fine powder, is mixed intimately with two parts of fluor-spar, and the mixture is heated with three or four times its weight of sulphuric acid, as long as any acid vapours are disengaged. The silicic acid of the mineral is attacked by hydrofluoric acid, and dissipated in the form of fluosilicic acid gas, while the alumina and lithia unite with sulphuric acid. After dissolving these salts in water, the solution is boiled with pure ammonia to precipitate the alumina:

it is then filtered and evaporated to dryness, and the dry mass heated to redness to expel the sulphate of ammonia. The residue is pure sulphate of lithia.

Prop.—Lithia, in its alkalinity, in forming a hydrate with water, and in its chemical relations, is closely allied to potassa and soda. It is distinguished from them by its greater neutralizing power, by forming sparingly soluble compounds with carbonic and phosphoric acids, and by its salts, when heated on platinum wire before the blowpipe, tinging the flame of a red colour. Also, when fused on platinum foil, it attacks that metal and leaves a dull yellow trace round the spot where it lay. It is distinguished from baryta, strontia, and lime, by forming soluble salts with sulphuric and oxalic acids, and from magnesia by its carbonate, though sparingly soluble in water, forming with it a solution which has an alkaline reaction. Its eq. is 14; symb. $L + O$, $\dot{L}$, or LO.

Chloride of Lithium.—It is readily obtained by dissolving lithia or its carbonate in hydrochloric acid. Like the chlorides of sodium and potassium, it yields by evaporation in a warm place colourless, anhydrous, cubic crystals, which differ from those chlorides in being very deliquescent, dissolving freely in alcohol as well as water, and in its alcoholic solution burning with a red flame.

Its eq. is 41·42; symb. $L + Cl$, or LCl.

The iodide and bromide of lithium have not been examined.

Fluoride of Lithium.—This is a fusible compound, prepared by dissolving lithia in hydrofluoric acid, and possesses about the same solubility in water as the carbonate.

CLASS I.

ORDER II.

METALLIC BASES OF THE ALKALINE EARTHS.

SECTION IV.

BARIUM.

Hist. and Prep.—Davy discovered *barium*, the metallic base of baryta, in the year 1808, by a process suggested by Berzelius and Pontin. It consists in forming carbonate of baryta into a paste with water, placing a globule of mercury in a little hollow made in its surface, and laying the paste on a platinum tray which communicated with the positive pole of a galvanic battery of 100 double plates, while the negative wire was in contact with the mercury. The baryta was decomposed, and its barium combined with mercury. This amalgam was then heated in a vessel free from air, by which means the mercury was expelled, and barium obtained in a pure form.

Prop.—A dark grey coloured metal, with a lustre inferior to cast iron. It is far denser than water, for it sinks rapidly in strong sulphuric acid. It attracts oxygen with avidity from the air, and in doing so yields a white powder, which is baryta. It effervesces strongly from the escape of hydrogen gas when thrown into water, and a solution of baryta is produced. It has hitherto been obtained in very minute quantities, and consequently its properties have not been determined with precision.

The eq. of barium, deduced from an analysis of the chloride by Berzelius and myself, is 68·7. Its symb. is Ba. The composition of its compounds described in this section is as follows:—

	Barium.			Equiv.	Formulæ.
Protoxide	68·7	1 eq.+Oxygen	8	1 eq.= 76·7	$Ba+O$ or BaO.
Peroxide	68·7	1 eq.+Ditto	16	2 eq.= 84·7	$Ba+2O$ or BaO_2.
Chloride	68·7	1 eq.+Chlorine	35·42	1 eq.=104·12	$Ba+Cl$ or $BaCl$.
Iodide	68·7	1 eq.+Iodine	126·3	1 eq.=195·0	$Ba+I$ or BaI.
Bromide	68·7	1 eq.+Bromine	78·4	1 eq.=147·1	$Ba+Br$ or $BaBr$.
Fluoride	68·7	1 eq.+Fluorine	18·68	1 eq.= 87·38	$Ba+F$ or BaF.
Sulphuret	68·7	1 eq.+Sulphur	16·1	1 eq.= 84·8	$Ba+S$ or BaS.

Protoxide of Barium.—Hist. and Prep.—Barytes, or *Baryta*, so called from the great density of its compounds, (from βαρυς, heavy,) was discovered in the year 1774 by Scheele. It is the sole product of the oxidation of barium in air or water. It may be prepared by decomposing nitrate of baryta at a red heat; or by exposing carbonate of baryta contained in a black-lead crucible to an intense white heat, a process which succeeds much better when the carbonate is intimately mixed with charcoal.

Prop.—A grey powder, the sp. gr. of which is about 4. It requires a very high temperature for fusion; has a sharp caustic alkaline taste, converts vegetable blue colours to green, and neutralizes the strongest acids. Its alkalinity, therefore, is equally distinct as that of potassa or soda; but it is much less caustic and less soluble in water than those alkalies. In pure alcohol it is insoluble. It has an exceedingly strong affinity for water. When mixed with that liquid it slakes in the same manner as quicklime, but with the evolution of a more intense heat, which, according to Döbereiner, sometimes amounts to incandescence. The result is a white bulky hydrate, fusible at a red heat, and which bears the highest temperature of a smith's forge without parting with its water. It is composed of 76·7 parts or 1 eq. of baryta, and 9 parts or 1 eq. of water.

Hydrate of baryta dissolves in three times its weight of boiling water, and in twenty parts of water at the temperature of 60° F. (Davy.) A saturated solution of baryta in boiling water deposits, in cooling, transparent, flattened prismatic crystals, which are composed, according to Phillips, of 76·7 parts or 1 eq. of baryta, and 90 parts or 10 eq. of water. Smith states, however, that the quantity of water amounts only to 81 parts or 9 eq. He has also pointed out the existence of a hydrate containing only 2 eq. of water; it is a white powder which is formed by exposing the crystallized hydrate to the temperature of a sand bath. (Phil. Mag. and An. vi. 53. and ix. 87.)

The aqueous solution of baryta is an excellent test of the presence of carbonic acid in the atmosphere or in other gaseous mixtures. The carbonic acid unites with the baryta, and a white insoluble precipitate, carbonate of baryta, subsides.

Baryta is distinguished from all other substances by the following characters. 1. By dissolving in water and forming an alkaline solution. 2. By all its soluble salts being precipitated as white carbonate of baryta by alkaline carbonates, and as sulphate of baryta, which is insoluble both in acid and alkaline solutions, by sulphuric acid or any soluble sulphate. 3. By the characters of chloride of barium, formed by the action of hydrochloric acid on baryta.

The readiest method of preparing the soluble salts of baryta is by dissolving the carbonate in dilute acid. All of its soluble salts are poisonous; and the carbonate, from being dissolved by the juices of the stomach, likewise acts as a poison. The sulphate, from its insolubility, is inert.

Its eq. is 76·7; symb. $Ba + O$, $\dot{Ba}$, or BaO.

Peroxide of Barium.—This oxide, which is used by Thenard in preparing peroxide of hydrogen, may be formed by conducting dry oxygen gas over pure baryta at a low red heat. A still easier process, given by Wöhler and Liebig, is to heat pure baryta to low redness in a platinum crucible, and then gradually to add chlorate of potassa in the ratio of about one part of the latter to four of the former. The oxygen of the chlorate goes over to the baryta, and chloride of potassium is generated. Cold water afterwards removes the chloride, and the peroxide of barium is left as a hydrate with 6 eq. of water, its formula being $BaO_2 + 6$ aq.

Chloride of Barium.—It is generated when chlorine gas is conducted over baryta at a red heat, oxyen gas being disengaged; but it is most conveniently prepared by dissolving carbonate of baryta in hydrochloric acid diluted with about three times its weight of water, or by decomposing a solution of sulphuret of barium with hydrochloric acid. On concentrating its solution, the chloride crystallizes on cooling in flat four-sided tables bevelled at the edges, very like crystals of heavy spar. These crystals consist of 104·12 parts or 1 eq. of chloride of barium, and 18 parts or 2 eq. of water, its formula being $BaCl + 2$ aq. They do not change in ordinary states of the air; but in a very dry atmosphere at 60° they lose all their water, and recover it again in a moist air. They are still more rapidly rendered anhydrous at 212°, and fusion ensues at a full red heat. They are insoluble in strong alcohol: 100 parts of water dissolve 43·5 at 60° and 78 at 222°, which is the boiling point of the solution. Its eq. is 104·12; symb. $Ba + Cl$, or $BaCl$.

Iodide of Barium.—This compound may be formed in the same way as iodide of potassium. It is very soluble in water, and crystallizes in small colourless needles, which deliquesce slightly. On exposure to the air a portion of carbonate of baryta is formed, and iodine set free, which probably forms a periodide of barium.

Its eq. is 159; symb. $Ba + I$, or BaI.

Bromide of Barium.—It was prepared by M. Henry, jun. who has examined it, by boiling protobromide of iron with moist carbonate of baryta in excess, evaporating the filtered solution, and heating the residue to redness. The product crystallizes by careful evaporation in white rhombic prisms, which have a bitter taste, are slightly deliquescent, and are soluble in water and alcohol.

Its eq. is 147·1; symb. $Ba + Br$, or $Ba\,Br$.

Fluoride of Barium.—On digesting recently precipitated and moist carbonate of baryta in hydrofluoric acid, carbonic acid is expelled, and fluoride of barium collects in the form of a white powder, which bears a red heat without decomposition. It is sparingly soluble in water, and by evaporation separates in crystalline grains. It is soluble in nitric and hydrochloric acids.

Its eq. is 87·38; symb. $Ba + F$, or BaF.

Sulphuret of Barium.—Prep.—This compound may be formed by transmitting dry hydrosulphuric acid gas over pure baryta at a red heat; and by the action of hydrogen gas or charcoal on sulphate of baryta. The easiest process is to mix sulphate of baryta in fine powder into a paste with an equal volume of fluor, place it in a hessian crucible on which a cover is luted, and expose it to a white heat for an hour or two, raising the temperature slowly. On pouring hot water on the ignited mass, the sulphuret of barium is dissolved, and may be separated from undecomposed sulphate and excess of charcoal by filtration.

Protosulphuret of barium is very soluble in hot water, and the solution if saturated deposits colourless crystals on cooling, which are sulphuret of barium with water of crystallization. The solution has a sulphurous odour, and absorbs oxygen and carbonic acid from the air, yielding carbonate and hyposulphite of baryta. Boiled with sulphur it yields a yellow solution, and contains a persulphuret of barium.

Sulphuret of barium supplies a ready mode of obtaining pure baryta and its salts, when the carbonate cannot be obtained. Thus its solution boiled with black oxide of copper until it ceases to precipitate a salt of lead black, yields pure baryta, which should be filtered while hot to separate the sulphuret of copper: it is apt to retain traces of oxide of copper. With a solution of carbonate of potassa, carbonate of baryta falls, and sulphuret of potassium remains in solution; and with hydrochloric acid it interchanges elements, by which hydrosulphuric acid and chloride of barium are formed. The sulphuret of barium is now much used in organic researches, particularly in purifying vegetable acids, such as malic acid (Liebig). Its eq. is 84·8; symb. $Ba + S$, or BaS.

SECTION V.

STRONTIUM.

Davy discovered the metallic base of strontia, called *strontium*, by a process analogous to that described in the last section. All that is known respecting its properties is, that it is a heavy metal, similar in appearance to barium, that it decomposes water with evolution of hydrogen gas, and oxidizes quickly in the air, being converted in both cases into strontia, which is the protoxide of the metal.

The eq. of strontium, deduced from the experiments of Stromeyer, is 43·8; its symb. Sr. The composition of its several compounds described in this section is as follows:—

	Strontium.				Equiv.	Formulæ.
Protoxide . .	43·8	1 eq.+Oxygen	8	1 eq.=	51·8	Sr+O or SO.
Peroxide . .	43·8	1 eq.+Do.	16	2 eq.=	59·8	Sr+2O or SO_2.
Chloride . .	43·8	1 eq.+Chlorine	35·42	1 eq.=	79·22	Sr+Cl or SrCl.
Iodide . . .	43·8	1 eq.+Iodine	126·3	1 eq.=	170·1	Sr+I or SrI.
Fluoride . .	43·8	1 eq.+Fluorine	18·68	1 eq.=	62·48	Sr+F or Srf.
Sulphuret . .	43·8	1 eq.+Sulphur	16·1	1 eq.=	59·9	Sr+S or SrS.

Protoxide of Strontium.—Hist.—From the close resemblance between baryta and strontia, these substances were once supposed to be identical. Crawford, however, and Sulzer noticed a difference between them; but the existence of strontia was first established with certainty in the year 1792 by Hope,* and the discovery was made about the same time by Klaproth.† It was originally extracted from strontianite, native carbonate of strontia, a mineral found at Strontian in Scotland; and hence the origin of the term *Strontites*, or *Strontia*, by which the earth itself is designated.

Prep. and Prop.—Pure strontia may be prepared from nitrate and carbonate of strontia, in the same manner as baryta. It resembles this earth in appearance, in infusibility, and in possessing distinct alkaline properties. It slakes when mixed with water, causing intense heat, and forming a white solid hydrate, which consists of 51·8 parts or 1 eq. of strontia, and 9 parts or 1 eq. of water. Hydrate of strontia fuses readily at a red heat. It is insoluble in alcohol. Boiling water dissolves it freely, and a hot saturated solution, on cooling, deposits transparent crystals in the form of thin quadrangular tables, which consist of 1 eq. of strontia and 10 eq. of water according to Phillips. Smith gives its composition to be $SrO + 9HO$. He also states that dried at 212° it becomes $SrO + HO$, and is anhydrous on exposure to a red heat. It requires 50 times its weight of water at 60° for solution, and twice its weight at 212° F. (Dalton.)

---

* Edin. Philos. Trans. iv. 3.

† Klaproth's Contributions, i.

The solution of strontia has a caustic taste and alkaline reaction. Like the solution of baryta, it is a delicate test of the presence of carbonic acid in air or other gaseous mixtures, forming with it the insoluble carbonate of strontia.

The salts of strontia are best prepared from the native carbonate. Like those of baryta, they are precipitated by alkaline carbonates, and by sulphuric acid or soluble sulphates. But sulphate of strontia is less insoluble than sulphate of baryta: on adding sulphate of soda in excess to a barytic solution, baryta cannot afterwards be found in the liquid by any precipitant; but when strontia is thus treated, so much sulphate of strontia remains in solution, that the filtered liquid yields a white precipitate with carbonate of soda. The salts of strontia are not poisonous; and most of them, when heated on platinum wire before the blowpipe, communicate to the flame a red tint.

Its eq. is 51·8; symb. $Sr + O$, $\dot{Sr}$, or SO.

Peroxide of Strontium is prepared in the same way as peroxide of barium, and, like it, is resolved by dilute acids into strontia and oxygen, the latter of which forms peroxide of hydrogen with the water.

Chloride of Strontium.—This compound is formed by processes similar to those for preparing chloride of barium, and crystallizes from its solution in colourless prismatic crystals, which deliquesce in a moist atmosphere, require only twice their weight of water at 60° for solution, and still less of boiling water, and are soluble in alcohol. The alcoholic solution, when set on fire, burns with a red flame. These characters afford a certain mode of distinguishing strontia from baryta. The crystals consist of 79·22 parts or 1 eq. of chloride of strontium, and 81 parts or 9 eq. of water, which are expelled by heat. The anhydrous chloride fuses at a red heat, and yields a white crystalline brittle mass on cooling.

Its eq. is 79·22; symb. $Sr + Cl$, or $SrCl$.

Iodide of Strontium may be prepared in the same manner as that of barium. It is very soluble in water, and fuses without decomposition in close vessels; but when heated to redness in the open air, iodine escapes, and strontia is generated.

Fluoride of Strontium is obtained in the same way as fluoride of barium, and is a white powder of sparing solubility.

Protosulphuret of Strontium is similar in its properties and mode of preparation to sulphuret of barium, and may be applied to similar uses. Strontium also combines with more than one equivalent of sulphur; but these compounds have not been examined.

SECTION VI.

CALCIUM.

The existence of calcium, the metallic base of lime, was demonstrated by Davy by a process similar to that described in the section on barium. It is of a whiter colour than barium or strontium, and is converted into lime by being oxidized. Its other properties are unknown.

According to the analysis of chloride of calcium by Berzelius, the eq. of calcium is 20·5; its symb. is Ca. Its compounds described in this section are composed as follows:—

	Calcium.			Equiv.	Formulæ.
Protoxide .	20·5	1 eq.+Oxygen	8	1 eq.= 28·5	$Ca+O$ or CaO.
Peroxide .	20·5	1 eq.+ . .	16·0	2 eq.= 36·5	$Ca+2O$ or CaO_2.
Chloride .	20·5	1 eq.+Chlorine	35·42	1 eq.= 55·92	$Ca+Cl$ or $CaCl$.
Iodide .	20·5	1 eq.+Iodine	126·3	1 eq.=146·8	$Ca+I$ or CaI.
Bromide .	20·5	1 eq.+Bromine	78·4	1 eq.= 98·9	$Ca+Br$ or $CaBr$.
Fluoride .	20·5	1 eq.+Fluorine	18·68	1 eq.= 39·18	$Ca+F$ or CaF.
Sulphuret .	20·5	1 eq.+Sulphur	16·1	1 eq.= 36·6	$Ca+S$ or CaS.
Bisulphuret .	20·5	1 eq.+ . . .	32·2	2 eq.= 52·7	$Ca+2S$ or CaS_2.
Quintosulphuret	20·5	1 eq.+ . . .	80·5	5 eq.=101	$Ca+5S$ or CaS_5.
Phosphuret .	20·5	1 eq.+Phosph.	15·7	1 eq.= 36·2	$Ca+P$ or CaP.

Protoxide of Calcium.—Prep.—This compound, commonly known by the name of *lime* and *quicklime*, is obtained by exposing carbonate of lime to a strong red heat, so as to expel its carbonic acid. If lime of great purity is required, it should be prepared from pure carbonate of lime, such as Iceland spar or Carrara marble; but in burning lime in lime-kilns for making mortar, common limestone is employed. The expulsion of carbonic acid is facilitated by mixing the carbonate with combustible substances, in which case carbonic oxide is generated. A current of air also greatly facilitates the burning of lime; for in close vessels it is hardly possible to expel the whole carbonic acid. The effect of a current of air is partly due to the diffusion of one gas in another.

Prop.—It is a brittle white earthy solid, the sp. gr. of which is about 2·3. It phosphoresces powerfully when heated to full redness, a property which it possesses in common with strontia and baryta. It is one of the most infusible bodies known ; fusing with difficulty, even by the heat of the oxy-hydrogen blowpipe. It has a powerful affinity for water, and the combination is attended with great increase of temperature, and formation of a white bulky hydrate, which is composed of 28·5 parts or 1 eq. of lime, and 9 parts or 1 eq. of water. The process of *slaking* lime consists in forming this hydrate, and the hydrate itself is called *slaked* lime. It differs from the hydrate of baryta in parting with its water at a red heat.

Hydrate of lime is dissolved very sparingly by water, and it is a singular fact, first noticed, I believe, by Dalton, that it is more soluble in cold than in hot water. Thus he found that one grain of lime requires for solution

778 grains of water . .	at 60° F.
972	130°
1270	212°

And, consequently, on heating a solution of *lime water*, which has been prepared in the cold, deposition of lime ensues. This fact was determined experimentally by Phillips, who has likewise observed that water at 32° is capable of dissolving twice as much lime as at 212° F. Owing to this circumstance pure lime cannot be made to crystallize in the same manner as baryta or strontia ; but Gay-Lussac succeeded in obtaining crystals of lime by evaporating lime water under the exhausted receiver of an air-pump by means of sulphuric acid. Small transparent crystals, in the form of regular hexahedrons, were deposited, which consist of water and lime in the same proportion as in the hydrate above mentioned.

Lime water is prepared by mixing hydrate of lime with water, agitating the mixture repeatedly, and then setting it aside in a well-stopped bottle until the undissolved parts shall have subsided. The substance called *milk* or *cream* of lime is made by mixing hydrate of lime with a sufficient quantity of water to give it the liquid form ;—it is merely lime water in which hydrate of lime is mechanically suspended.

Lime water has a harsh acrid taste, and converts vegetable blue colours to green.—It agrees, therefore, with baryta and strontia in possessing distinct alkaline properties. Like the solutions of these earths, it has a strong affinity for carbonic acid, and forms with it an insoluble carbonate. On this account lime water should be carefully protected from the air. For the same reason, lime water is rendered turbid by a solution of carbonic acid; but on adding a large quantity of the acid, the transparency of the solution is completely restored, because carbonate of lime is soluble in an excess of carbonic acid. The action of this acid on the solutions of baryta and strontia is precisely similar.

The salts of lime, which are easily prepared by the action of acids on pure marble, are in many respects similarly affected by reagents, as those of baryta and strontia. They are precipitated, for example, by alkaline carbonates. Sulphuric acid and soluble sulphates likewise precipitate lime from a moderately strong solution. But sulphate of lime has a considerable degree of solubility. Thus, a dilute solution of a salt of lime is not precipitated at all by sulphuric acid; and when the sulphate of lime is separated, it may be redissolved by the addition of nitric acid.

The most delicate test of the presence of lime is oxalate of ammonia or potassa; for of all the salts of lime, the oxalate is the most insoluble in water. This serves to distinguish lime from most substances, though not from baryta and strontia; because the oxalates of baryta and strontia, especially the latter, are likewise sparingly soluble.—All these oxalates dissolve readily in water acidulated with nitric or hydrochloric acid. It is distinguished from baryta and strontia by the fact, that nitrate of lime yields prismatic crystals by evaporation, is deliquescent in a high degree, and very soluble in alcohol; while the nitrates of baryta and strontia crystallize in regular octohedrons, or segments of the octohedron, undergo no change on exposure to the air, except when it is very moist, and do not dissolve in pure alcohol.

The salts of lime, when heated before the blowpipe, or when their solutions in alcohol are set on fire, communicate to the flame a dull brownish-red colour.

Its eq. is 28·5; symb. $Ca + O$, $\dot{Ca}$, or CaO.

Peroxide of Calcium.—This oxide is prepared in the same way as peroxide of barium, and is similar to it in its properties.

Chloride of Calcium.—This compound exists in sea-water and in many saline springs, is the residue of the process for preparing ammonia, and is readily formed by dissolving marble or chalk in hydrochloric acid. On evaporating its solution to the consistence of a syrup, the chloride crystallizes on cooling in irregular, colourless prismatic crystals, which consist of 55·92 parts or 1 eq. of chloride of calcium and 54 parts or 6 eq. of water. By heat it loses its water, and at a gentle red heat fuses; but on exposure to the air it rapidly recovers its water of crystallization and then deliquesces. Owing to its strong affinity for water, it is much used for frigorific mixtures with snow; but for this purpose the hydrous chloride is preferable, as prepared by evaporating its solution so far, that the whole becomes a solid mass on removal from the fire, reducing it when cold quickly to powder, and preserving it in bottles closed with great care. It is also used for drying gases, and ethereal and oily liquids, and, in organic analysis, to absorb the water formed, and thus determine the amount of hydrogen. Chloride of calcium is very soluble in alcohol, and forms with it a definite compound.

Its eq. is 55·92; symb. Ca + Cl, or CaCl.

Iodide of Calcium.—This compound may be prepared by digesting hydrate of lime with protiodide of iron. It is deliquescent and very soluble in water, sustains a red heat unchanged in close vessels, but when heated in the open air its iodine is replaced by oxygen, and lime remains. The solution of iodide of calcium dissolves a large quantity of iodine, and on evaporating the brown solution in vacuo above a vessel with dry carbonate of potassa, a periodide of calcium crystallizes in large black prisms of a metallic lustre.

Its eq. is 46·8; symb. Ca + I, or CaI.

Bromide of Calcium.—It was prepared by Henry by digesting hydrate of lime with a solution of protobromide of iron, and crystallizes in acicular crystals which are very deliquescent, and extremely soluble in alcohol and water. It is very analogous in taste and properties to chloride of calcium, fuses by heat, but in open vessels suffers partial decomposition.

Its eq. is 98·9; symb. Ca + Br, or CaBr.

Fluoride of Calcium.—*Hist. and Prep.*—This is a natural product, which frequently accompanies metallic ores, especially those of lead and tin, often occurs in cubic crystals, and is well known under the name of *fluor* or *Derbyshire spar*. The crystals found in the lead mines of Derbyshire are remarkable for the largeness of their size, the regularity of their form, and the variety and beauty of their colours. It may be prepared artificially by digesting moist, recently precipitated, carbonate of lime in an excess of hydrofluoric acid; or by mixing a solution of chloride of calcium with fluoride of potassium or sodium. As prepared in the latter mode, it is a bulky gelatinous mass, which it is very difficult to wash; whereas the former method gives it in the state of a granular white powder, which may be washed with ease.

Prop.—Fluoride of calcium fuses at a red heat without farther change. It is insoluble in water, slightly soluble in hot diluted hydrochloric acid, and is decomposed by sulphuric acid aided by gentle heat. It is in a small degree decomposed by boiling nitric acid. Fused with carbonate of potassa, carbonate of lime and fluoride of potassium are generated.

Fluor-spar is much used in forming vases, as a flux in metallurgic processes, and in the preparation of hydrofluoric acid.

Its eq. is 39·18; symb. $Ca + F$, or CaF.

Protosulphuret of Calcium.—*Prep.*—By reduction from the sulphate by hydrogen or charcoal, and when pure is white with a reddish tint, and is very sparingly soluble in water. It has the property, in common with sulphuret of barium, of being phosphorescent after exposure to light, and appears to be the essential ingredient of Canton's Phosphorus.

When 3 parts of slaked lime, 1 of sulphur, and 20 of water are boiled together for an hour, and the solution, without separation from the sediment, is set aside in a corked flask for a few days, a copious deposite of orange-coloured crystals are deposited, which, when slowly formed, are flat quadrilateral prisms. These, from the analysis of Herschel, appear to be bisulphuret of calcium with 3 eq. of water. They are decomposed by exposure to the air, and are of sparing solubility in water.

When either of the foregoing sulphurets is boiled in water along with sulphur, a yellow solution is formed containing calcium combined with 5 eq. of sulphur.

Phosphuret of Calcium.—It is formed by passing the vapour of phosphorus over fragments of quicklime at a low red heat, when a brown matter is formed consisting of phosphate of lime and phosphuret of calcium. When put into water, mutual decomposition ensues, and phosphuretted hydrogen, hypophosphorous acid, and phosphoric acid are generated.

SECTION VII.

MAGNESIUM.

Hist. and Prep.—The galvanic researches of Davy demonstrated the existence of magnesium, though he obtained it in a quantity too minute for determining its properties. It was prepared by Bussy, in the year 1830, by the action of potassium on chloride of magnesium. For this purpose five or six pieces of potassum, of the size of peas, were introduced into a glass tube, the sealed extremity of which was bent into the form of a retort, and upon the potassium were laid fragments of chloride of magnesium. The latter being then heated to near its point of fusion, a lamp was applied to the potassium, and its vapour transmitted through the mass of heated chloride. Vivid incandescence immediately took place, and on putting the mass, after cooling, into water, the chloride of potassium with undecomposed chloride of magnesium was dissolved, and metallic magnesium subsided. These results have been since confirmed by Liebig. (An. de Ch. et Ph. xlvi. 435.)

Prop.—Magnesium has a brilliant metallic lustre, and a white colour like silver, is very malleable, and fuses at a red heat. Moist air oxidizes it superficially; but it undergoes no change in a dry air, and may be boiled in water without oxidation. Heated to redness in air or oxygen gas, it burns with brilliancy, yielding magnesia; and it inflames spontaneously in chlorine gas. It is readily dissolved by dilute acids with disengagement of hydrogen, and the solution is found to contain a pure salt of magnesia.

The eq. of magnesium, inferred by Berzelius from the quantity of sulphate obtained from a known weight of pure magnesia, is 12·7; its symb. is Mg. Its compounds described in this section are composed as follows:—

	Magnesium.			Equiv.	Formulæ.
Protoxide .	12·7	1 eq.+Oxygen	8	1 eq.= 20·7	$Mg+O$ or MgO.
Chloride .	12·7	1 eq.+Chlorine	35·42	1 eq.= 48·12	$Mg+Cl$ or $MgCl$.
Iodide . .	12·7	1 eq.+Iodine	126·3	1 eq.=139	$Mg+I$ or MgI.
Bromide .	12·7	1 eq.+Bromine	78·4	1 eq.= 91·1	$Mg+Br$ or $MgBr$.
Fluoride .	12·7	1 eq.+Fluorine	18·68	1 eq.= 31·38	$Mg+F$ or MgF.

Protoxide of Magnesium. — *Prep.*—This, the only known oxide of magnesium, commonly known by the name of *magnesia*, is best obtained by exposing carbonate of magnesia to a very strong red heat, by which its carbonic acid is expelled. It is a white friable powder, of an earthy appearance; and when pure it has neither taste nor odour. Its sp. gr. is about 2·3, and it is exceedingly infusible. It has a weaker affinity than lime for water; for though it forms a hydrate when moistened, the combination is effected with hardly any disengagement of heat, and the product is readily decomposed by a red heat. According to the analysis of Stromeyer, the native hydrate contains 1 eq. of each of its constituents; and the results of the analyses of Berzelius and Fyfe accord very nearly with this proportion. It has generally been thought that magnesia formed several hydrates; but the recent observations of Rees indicate that the artificial hydrates have the same composition as the native (Phil. Mag. and An. x. 454).

Prop.—Very sparingly soluble in water. According to Fyfe, it requires 5142 times its weight of water at 60°, and 36,000 of boiling water for solution. The resulting liquid does not change the colour of violets; but when pure magnesia is put upon moistened turmeric paper, it causes a brown stain. From this there is no doubt that the inaction of magnesia with respect to vegetable colours, when tried in the ordinary mode, is owing to its insolubility.—It possesses the still more essential character of alkalinity, that, namely, of forming neutral salts with acids, in an eminent degree. It absorbs both water and carbonic acid when exposed to the atmosphere, and therefore should be kept in well-closed phials.

Magnesia is characterized by the following properties. With nitric and hydrochloric acids it forms salts which are soluble in alcohol, and exceedingly deliquescent. The sulphate of magnesia is very soluble in water, a circumstance by which it is distinguished from the other alkaline earths. Magnesia is precipitated from its salts as a bulky hydrate by the pure alkalies. It is precipitated as carbonate of magnesia, by the carbonates of potassa and soda; but the bicarbonates, and the common carbonate of ammonia, do not precipitate it in the cold. If moderately diluted, the salts of magnesia are not precipitated by oxalate of ammonia. By means of this reagent magnesia may be both distinguished and separated from lime.

Its eq. is 20·7; symb. $Mg + O$, $\dot{Mg}$, or MgO.

Chloride.—This compound may be prepared by transmitting dry chlorine gas over a mixture of magnesia and charcoal at a red heat;

but Liebig has given an easier process, which consists in dissolving magnesia in hydrochloric acid, evaporating to dryness, mixing the residue with its own weight of hydrochlorate of ammonia, and projecting the mixture in successive portions into a platinum crucible at a red heat. As soon as the ammoniacal salt is wholly expelled, the fused chloride of magnesium is left in a state of tranquil fusion, and on cooling becomes a transparent colourless mass, which is highly deliquescent, and is very soluble in alcohol and water.

Its eq. is 48·12; symb. MgCl.

Iodide of magnesium is obtained by dissolving magnesia in hydriodic acid, is very soluble in water, and is only known in solution.

Bromide of magnesium, obtained by dissolving magnesia in hydrobromic acid, crystallizes in small acicular prisms, which have a sharp taste, are deliquescent, and very soluble in water and alcohol. It is decomposed by a strong heat.

Fluoride of magnesium is prepared by digesting magnesia in hydrofluoric acid in excess. It is insoluble in water and in excess of hydrofluoric acid, and bears a red heat without decomposition.

CLASS I.

ORDER III.

METALLIC BASES OF THE EARTHS.

SECTION VIII.

ALUMINIUM.

Hist.—THAT alumina is an oxidized body was proved by Davy, who found that potassa is generated when the vapour of potassium is brought into contact with pure alumina heated to whiteness; and it was inferred, chiefly by analogical reasoning, to be a metallic oxide. The propriety of this inference has been demonstrated by Wöhler, who has procured *aluminium*, the metallic base of alumina, in a pure state (Edinburgh Journal of Science, No. xvii. 178).

Prep.—Depends on the property which potassium possesses, of decomposing the chloride of aluminium. Decomposition is effected by aid of a moderate increase of temperature; but the action is so violent, and accompanied with such intense heat, that the process cannot be safely conducted in glass vessels. Wöhler succeeded with a platinum crucible, retaining the cover in its place by a piece of wire. The heat developed during the action was so great, that the crucible, though but gently heated externally, suddenly became red hot. The platinum is scarcely attacked during the process; but to prevent the possibility of error from this source, the decomposition was also effected in a crucible of porcelain. The potassium employed for the purpose should be quite free from carbon, and the quantity operated on at one time not exceed the size of ten peas. The heat was applied by means of a spirit lamp, and continued until the action was completed. The proportion of the materials requires to be carefully adjusted; for the potassium should be in such quantity as to prevent any chloride of aluminium from subliming during the process, but not so much as to yield an alkaline solution when the product is put into water. The matter contained in the crucible at the close of the operation is in general completely fused, and of a dark grey colour. When *quite cold*, the crucible is put into a large glass full of water, in which the saline matter is dissolved, with slight disengagement of hydrogen of an offensive odour; and a grey powder separates, which on close inspection, especially in sunshine, is found to consist solely of minute scales of metal. These scales, after being well washed with *cold* water, are pure aluminium. The saline matter removed by water is chloride of potassium, and a considerable quantity of chloride of aluminium.

Prop.—As thus formed, it is a grey powder, very similar to that of platinum. It is generally in small scales or spangles of a metallic lustre; and sometimes small, slightly coherent, spongy masses are observed, which in some places have the lustre and white colour of tin. The same appearance is rendered perfectly distinct by pressure on steel, or in an agate mortar; so that the lustre of aluminium is decidedly metallic. In its fused state it is a conductor of electricity, though it does not possess this property when in the form of powder. This remark, of a metal conducting the electric fluid in one state and not in another, is very instructive; and Wöhler observed an instance of the same kind in iron, which in the state of fine powder is a non-conductor of electricity.

Aluminium requires for fusion a temperature higher than that at which cast iron is liquefied. When heated to redness in the open air, it takes fire and burns with vivid light, yielding aluminous earth of a white colour, and of considerable hardness. Sprinkled in powder in the flame of a candle, brilliant sparks are emitted, like those given off during the combustion of iron in oxygen gas. When heated to redness in a vessel of pure oxygen gas, it burns with an exceedingly vivid light, and emission of intense heat. The resulting alumina is partially vitrified, of a yellowish colour, and equal in hardness to the native crystallized aluminous earth, corundum. Heated to near redness in an atmosphere of chlorine, it takes fire, and chloride of aluminium is sublimed.

Aluminium is not oxidized by water at common temperatures, nor is its lustre tarnished by lying in water during its evaporation. On heating the water to near its boiling point, oxidation of the metal commences, with feeble disengagement of hydrogen gas, the evolution of which continues even long after cooling, but at length wholly ceases. The oxidation, however, is very slight; and even after continued ebullition, the smallest particles of aluminium appear to have suffered scarcely any change.

It is not attacked by concentrated sulphuric or nitric acid at common temperatures. In the former, with the aid of heat, it is rapidly dissolved with disengagement of sulphurous acid gas. In dilute hydrochloric and sulphuric acid, and also in a dilute solution of potassa, it dissolves with evolution of hydrogen gas. Ammonia produces a similar effect, and dissolves a large quantity of alumina. The hydrogen gas which makes its appearance is of course derived from water, the oxygen of which combines with the metal so as to constitute alumina.

From the composition of the sulphates of alumina, ascertained by Berzelius, Stromeyer, and Phillips, the equivalent of alumina may be estimated either at 25·7, or at 51·4, twice that number. Now chemists have no direct means of discovering the atomic constitution of alumina, inasmuch as aluminium combines with oxygen and most other elements in one proportion only. Thomson assumes alumina to consist of single atoms of its elements: but most chemists, seeing that alumina has little analogy to protoxides in its modes of combining, but that in its form and all its chemical relations it closely resembles peroxide of iron, have inferred that the simplest molecule of alumina contains 2 atoms of aluminium and 3 atoms of oxygen. On this supposition 51·4 must be the eq. of alumina, and 13·7 that of aluminium; its symb. Al. The composition of its compounds described in this section is the following :—

	2 eq. Aluminium.				Equiv.	Formulæ.
Sesquioxide	26·4 +	oxygen	24	3 eq. =	51·4	$2Al+3O$ or Al_2O_3.
Sesquichloride	26·4 +	chlorine	106·26	3 eq. =	132·66	$2Al+3Cl$ or Al_2Cl_3.
Sesquisulphuret	26·4 +	sulphur	48·3	3 eq. =	74·7	$2Al+3S$ or Al_2S_3.
Sesquiphosphuret	26·4 +	phosphs.	47·1	3 eq. =	73·5	$2Al+3P$ or Al_2P_3.
Sesquiseleniuret	26·4 +	selenium	118·2	3 eq. =	144·6	$2Al+3Se$ or Al_2Se_3.

The composition of the four last compounds is matter of inference from the change which they respectively undergo by the action of water.

Sesquioxide of Aluminium.—Hist. and Prep.—The only known oxide of this metal, and is commonly called *alumina* or *aluminous earth*. It is one of the most abundant productions of nature. It is found in every region of the globe, and in rocks of all ages, being a constituent of the oldest primary mountains, of the secondary strata, and of the most recent alluvial depositions. The different kinds of clay of which bricks, pipes, and earthenware are made, consist of hydrate of alumina in a greater or less degree of purity. Though this earth commonly appears in rude amorphous masses, it is sometimes found beautifully crystallized.—The ruby and the sapphire, two of the most beautiful gems with which we are acquainted, are composed almost solely of alumina.

Pure alumina is prepared from alum, sulphate of alumina and potassa. This salt, as purchased in the shops, is frequently contaminated with peroxide of iron, and consequently unfit for many chemical purposes; but it may be separated from this impurity by repeated crystallization. Its absence is proved by the alum being soluble without residue in a solution of pure potassa; whereas when peroxide of iron is present, it is either left undissolved in the first instance, or deposited after a few hours in yellowish brown flocks. Any quantity of purified alum is dissolved in four or five times its weight of boiling water, a slight excess of carbonate of potassa added, and after digesting for a few minutes, the bulky hydrate of alumina is collected on a filter, and well washed with hot water. It is necessary in this operation to digest and employ an excess of alkali; since otherwise the precipitate would retain some sulphuric acid in the form of a subsulphate. But the alumina, as thus prepared, is not yet quite pure; for it retains some of the alkali with such force, that it cannot be separated by the action of water. For this reason the precipitate must be re-dissolved in dilute hydrochloric acid, and thrown down by means of pure ammonia or its carbonate. This precipitate, after being well washed and exposed to a white heat, yields pure anhydrous alumina. Ammonia cannot be employed for precipitating aluminous earth directly from alum, because sulphate of alumina is not completely decomposed by this alkali (Berzelius). Liebig precipitates alum with an excess of chloride of barium, evaporates the filtered liquid to dryness, and ignites the residue. Water now dissolves the chlorides of potassium and barium, and leaves alumina as a white powder, very easily washed. The washing of the hydrate, in the process first described, is a most tedious operation. An easier process, proposed by Gay-Lussac, is to expose sulphate of alumina and ammonia to a strong heat, so as to expel the ammonia and sulphuric acid.

Prop.—Alumina has neither taste nor smell, and is quite insoluble in water. It is very infusible, though less so than lime or magnesia. It has a powerful affinity for water, attracting moisture from the atmosphere with avidity; and for a like reason, it adheres tenaciously to the tongue when applied to it. Mixed with a due proportion of water, it yields a soft cohesive mass, susceptible of being moulded into regular forms, a property upon which depends its employment in the art of pottery. When once moistened, it cannot be rendered anhydrous, except by exposure to a full white heat; and in proportion as it parts with water, its volume diminishes. Owing to its insolubility, it does not affect the blue colour of plants. It appears to possess the properties both of an acid and of an alkali:—of an acid, by uniting with alkaline bases, such as potassa, lime, and baryta;—and of an alkali, by forming salts with acids. In neither case, however, are its soluble compounds neutral with respect to test paper.

Alumina most probably forms several different hydrates with water, and two have been described by Thomson. One of these, apparently composed of 6 eq. of water to one of alumina, so that its formula is $Al_2O_3 + 6$ aq. was procured by exposing precipitated alumina for the space of two months to a dry air, the temperature of which did not exceed 60°. The other is a terhydrate prepared by drying the preceding at a heat of about 100°, and its formula is therefore $Al_2O_3 + 3$ aq. The mineral called Gibbsite has a similar composition.

Alumina is easily recognised by the following characters. 1. It is separated from acids, as a hydrate, by all the alkaline carbonates and by pure ammonia. 2. It is precipitated by pure potassa or soda, but the precipitate is completely re-dissolved by an excess of the alkali. Its eq. is 51·4; symb. $2Al + 3O$, $\underline{\dddot{Al}}$, or Al_2O_3.

Sesquichloride of Aluminium.—Hist.—Oersted discovered this compound by transmitting dry chlorine gas over a mixture of alumina and charcoal heated to redness. By acting on this substance with an amalgam of potassium and expelling the mercury by heat, he obtained metallic matter, which he believed to be aluminium; but not having leisure to pursue the inquiry himself, he requested Wöhler to investigate the subject. Wöhler did not arrive at any satisfactory conclusion by the method suggested by Oersted; but met with complete success by means of pure potassium, as already described.

Prep.—To procure chloride of aluminium, Wöhler precipitated aluminous earth from a hot solution of alum by means of potassa, and mixed the hydrate, when dry, with pulverized charcoal, sugar, and oil, so as to form a thick paste, which was heated in a covered crucible until all the organic matter was destroyed. By this means the alumina was brought into a state of intimate mixture with finely divided charcoal, and while yet hot, was introduced into a tube of porcelain, fixed in a convenient furnace. After expelling atmospheric air from the interior of the apparatus by a current of dry chlorine gas, the tube was brought to a red heat. The formation of chloride of aluminium then commenced, and continued, with disengagement of carbonic oxide gas, during an hour and a half, when the tube became impervious from sublimed chloride of aluminium collected within it. The process was then necessarily discontinued.

Prop.—As thus formed, chloride of aluminium is of a pale greenish yellow colour, partially translucent, and of a highly crystalline lamellated texture, somewhat like talc, but without regular crystals. On exposure to the air, it fumes slightly, emits an odour of hydrochloric acid gas, and, deliquescing, yields a clear liquid. When thrown into water, it is speedily dissolved with a hissing noise; and so much heat is evolved, that the water, if in small quantity, is brought into a state of brisk ebullition. The solution is a true hydrochlorate of alumina, formed by decomposition of water; for when gently evaporated, hydrochloric acid escapes, and alumina is gradually deposited. According to Oersted it is volatile at a temperature a little higher than 212°, and fuses nearly at the same degree.

Sesquisulphuret of Aluminium.—Sulphur may be distilled from aluminium without combining with it; but if a piece of sulphur is dropped on aluminium when strongly incandescent, so that it may be enveloped in an atmosphere of the vapour of sulphur, the union is effected with vivid emission of light. The resulting sulphuret is a partially vitrified, semi-metallic mass, which acquires an iron-black metallic lustre when burnished. Applied to the tongue, it excites a pricking warm taste of hydrosulphuric acid. When put into pure water, or on exposure to the air, it is resolved, by an interchange of elements, into alumina and hydrosulphuric acid, the latter escaping as gas. It is to be presumed that

1 eq. Sulphuret and 3 eq. Water yield 1 eq. Alumina and 3 eq. Hydrosulph. Acid.
Al_2S_3 $3HO$ Al_22O_3 $3HS$

Wöhler finds that sulphuret of aluminium cannot be generated by the action of hydrogen gas on sulphate of alumina at a red heat; for in that case all the acid is expelled, without the aluminous earth being reduced.

Sesquiphosphuret of Aluminium.—When aluminium is heated to redness in contact with the vapour of phosphorus, it takes fire, and emits a brilliant light. The product is described by Wöhler as a blackish grey pulverulent mass, which by friction acquires a dark grey metallic lustre, and in the air smells instantly of phosphuretted hydrogen. By the action of water alumina and phosphuretted hydrogen gas are generated, but the latter is not spontaneously inflammable. The effervescence is less rapid than with the sulphuret, but is increased by heat.

Sesquiseleniuret of Aluminium.—This compound is formed, with disengagement of heat and light, by heating to redness a mixture of selenium and aluminium. The product is black and pulverulent, and assumes a dark metallic lustre when rubbed. In the air it emits a strong odour of hydroselenic acid; and this gas is rapidly disengaged by the action of water, which is speedily reddened by the separation of selenium.

SECTION IX.

GLUCINIUM, YTTRIUM, THORIUM, ZIRCONIUM.

GLUCINIUM.

Glucina,[*] which was discovered by Vauquelin in the year 1798, has hitherto been found only in three rare minerals, the euclase, beryl, and emerald. It is the only oxide of a metal which Wöhler succeeded in preparing in the year 1828 by a process exactly similar to that described in the last section. Chloride of glucinium is readily attacked by potassium when heated with the flame of a spirit-lamp, and the decomposition is attended with intense heat. After removing the resulting chloride of potassium by cold water, the glucinium appears in the form of a greyish black powder, which acquires a dark metallic lustre by burnishing. It may be exposed to air and moisture, or be even boiled in water, without oxidation. When heated in the open air, it takes fire and burns with a most vivid light; and in oxygen gas the combustion is attended with extraordinary splendour. The product in both cases is glucina, which is not at all fused by the intense heat that accompanied its formation. The metal is readily oxidized and dissolved in sulphuric, nitric, or hydrochloric acid with the aid of heat; and the same ensues, with disengagement of hydrogen gas, in solution of potassa. It is not attacked, however, by pure ammonia. When moderately heated in chlorine gas, it burns with great splendour, and a crystallized chloride sublimes. Similar phenomena ensue in the vapour of bromine and iodine; and it unites readily with sulphur, selenium, phosphorus, and arsenic. (Phil. Mag. and Annals, v. 392.)

According to the experiments of Berzelius, glucina contains 31·154 per cent. of oxygen, and consequently its eq. is 26·5 on the supposition that its constitution is similar to that of alumina, with which it is closely associated both in nature and in many of its properties. Its symb. is G.

Oxide of Glucinium or Glucina.—Prep.—This oxide is commonly prepared from beryl, in which it exists to the extent of about 14 per cent. combined with silicic acid and alumina. In order to procure it in a separate state, the mineral is reduced to an exceedingly fine powder, mixed with three times its weight of carbonate of potassa, and exposed to a strong red heat for half an hour, so that the mixture may be fused. The mass is then dissolved in dilute hydrochloric acid, and the solution evaporated to perfect dryness; by which means the silicic acid is rendered quite insoluble. The alumina and glucina are then redissolved in water acidulated with hydrochloric acid, and thrown down together by pure ammonia. The precipitate, after being well washed, is macerated with a large excess of carbonate of ammonia, by which glucina is dissolved; and on boiling the filtered liquid, carbonate of glucina subsides. By means of a red heat its carbonic acid is entirely expelled.

Another process has been recommended by Berthier, who directs the beryl to be mixed in fine powder with its own weight of marble, and the mixture to be exposed in a crucible to a strong heat. In this manner a glass is obtained, which when in fine powder is attached freely by hydrochloric or sulphuric acid. From this solution the glucina may be obtained as before.

Prop.—Glucina is a white powder, which has neither taste nor odour, and is quite insoluble in water. Its sp. gr. is 3. Vegetable colours are not affected by it. The salts which it forms with acids have a sweetish taste, a circumstance which distinguishes glucina from other earths, and from which its name is derived (from γλυϰυς, sweet).

Glucina may be known chemically by the following characters. 1. Pure potassa or soda precipitates glucina from its salts, but an excess of the alkali redissolves it. 2. It is precipitated permanently by pure ammonia as a hydrate, and by fixed alkaline carbonates as a carbonate of glucina. 3. It is dissolved completely by a cold solution of carbonate of ammonia, and is precipitated from it by boiling. By means of this property, glucina may be both distinguished and separated from alumina.

Its eq. is 77; symb. $2G + 3O$, $\underline{\dddot{G}}$, or G_2O_3.

YTTRIUM.

Yttrium is the metallic base of an earth which was discovered in the year 1794 by Professor Gadolin, in a mineral found at Ytterby in Sweden, from which it received the name of *Yttria.* The metal itself was prepared by Wöhler in 1828 by a process similar to that above described. Its texture, by which it is distinguished from glucinium and aluminium, is scaly, its colour greyish-black, and its lustre perfectly metallic. In colour and lustre it is inferior to aluminium, bearing in these respects nearly the same relation to that metal, that iron does to tin. It is a brittle metal, while aluminium is ductile. It is not oxidized either in air or water; but when heated to redness, it burns with splendour even in atmospheric air, and with far greater brilliancy in oxygen gas. The product, yttria, is white, and shows unequivocal marks of fusion. It dissolves in sulphuric acid, and also, though less readily, in solution of potassa; but it is not attacked by ammonia. It combines with sulphur, selenium, and phosphorus. (Phil. Mag. and Annals, v. 393.)

The salts of yttria have in general a sweet taste, and the sulphate and several others have an amethyst colour. It is precipitated as a hydrate by the pure alkalies, and is not redissolved by an excess of the precipitant; but alkaline carbonates, especially that of ammonia, dissolve it in the cold, though less freely than glucina, and carbonate of yttria is precipitated by boiling. Of all the earths it bears the closest resemblance to glucina; but it is readily distinguished from it by the colour of its sulphate, by its insolubility in pure potassa, and by yielding a precipitate with ferrocyanuret of potassium (Berzelius). The eq. of yttrium, as deduced by Berzelius, is 32·2; and that of yttria, which is probably a protoxide, is 40·2.

The symb. of the metal is Y; of its oxide $Y + O$, $\dot{Y}$, or YO.

THORIUM.

The earthy substance formerly called *thorina* was found by Berzelius to be phosphate of yttria; but in 1828 he discovered a new earth, so similar in some respects to what was formerly called thorina, that he applied this term to the new substance. The metallic base of thorina (thorium) was procured by the action of potassium on chloride of thorium, the decomposition being accompanied with a slight detonation. On washing the mass, thorium is left in the form of a heavy metallic powder, of a deep leaden-grey colour; and when pressed in an agate mortar, it acquires metallic lustre and an iron-grey tint. Thorium is not oxidized either by hot or cold water; but when gently heated in the open air it burns with great brilliancy, comparable to that of phosphorus burning in oxygen. The resulting thorina is as white as snow, and does not exhibit the least trace of fusion. It is not attacked by caustic alkalies at a boiling heat; is scarcely at all acted on by nitric acid, and very slowly by the sulphuric, but it is readily dissolved with disengagenent of hydrogen gas by hydrochloric acid.

Thorina.—Hist. and Prep.—Procured from a rare Norwegian mineral, now called *thorite*, which was sent to Berzelius by Esmark. It constitutes 57·91 per cent. of the mineral, and occurs in the form of a hydrated silicate of thorina. In order to prepare thorina, the mineral is reduced to powder, and digested in hydrochloric acid; when a gelatinous mass is formed, from which silicic acid is separated by evaporating to dryness, and dissolving the soluble parts in dilute acid. The solution is then freed from lead and tin, which occur in thorina along with several impurities, by hydrosulphuric acid, and the earths are thrown down by pure ammonia. The precipitate, after being well washed, is dissolved in dilute sulphuric acid, and the solution evaporated at a high temperature till only a small quantity of fluid remains. During the evaporation the greater part of the thorina is deposited as a sulphate; and on decanting the remaining fluid, washing the residue, and heating it to redness, pure thorina remains. (An. de Ch. et Ph. xliii. 5.)

Prop.—Thorina, when formed by the oxidation of thorium, or after being strongly heated, is a white earthy substance, of sp. gr. 9·402, and insoluble in all the acids except the sulphuric; and it dissolves even in that with difficulty. It is precipitated from its solutions by the caustic alkalies as a hydrate, and in this state absorbs carbonic acid from the atmosphere, and dissolves readily in acids. All the alkaline carbonates dissolve the hydrate, carbonate, and sub-salts of thorina. Its exact composition is not known; but its eq. is about 67·6.

Thorina is distinguished from alumina and glucina by its insolubility in pure potassa; from yttria by forming with sulphate of potassa a double salt which is quite insoluble in a cold saturated solution of sulphate of potassa; and from zirconia by the circumstance that this earth, after being precipitated from a hot solution of sulphate of potassa, is almost insoluble in water and the acids. Thorina is precipitated, also, by ferrocyanuret of potassium, which does not separate zirconia from its solutions. Berzelius has remarked that sulphate of thorina is much more soluble in cold than in hot water, so that a cold saturated solution becomes turbid when heated, and in cooling recovers its transparency.

Chloride of thorium is readily prepared by carbonizing an intimate mixture of thorina and sugar in a covered platinum crucible, and then exposing the residue at a red heat in a porcelain tube to a current of dry chlorine. The chloride, possessing but little volatility, collects in the tube just beyond the ignited part in the form of a partially fused, crystalline, white mass. It is soluble in water with considerable rise of temperature.

When thorium is heated in the vapour of sulphur, the phenomena of combustion ensue with the same brilliancy as in air, and a sulphuret results. A phosphuret may be formed by a similar process.

ZIRCONIUM.

Hist and Prep.—The experiments of Davy proved zirconia to be an oxidized body, and afforded a presumption that its base, *zirconium*, is of a metallic nature; but Berzelius first obtained the metal in 1824 by heating with a spirit-lamp a mixture of potassium and the double fluoride of zirconium and potassium, carefully dried in a tube of glass or iron. The reduction takes place at a temperature below redness, without emission of light; and the mass is washed with boiling water, and afterwards digested for some time in dilute hydrochloric acid. The residue is pure zirconium.

Prop.—Zirconium, thus obtained, is in the form of a black powder, which may be boiled in water without being oxidized, and is attacked with difficulty by sulphuric, hydrochloric, or nitro-hydrochloric acids; but it is dissolved readily, and with disengagement of hydrogen gas, by hydrofluoric acid. Heated in the open air, it takes fire at a temperature far below incandescence, burns brightly, and is converted into zirconia. Its metallic nature seems somewhat questionable. It may indeed be pressed out into thin shining scales of a dark grey colour, and of a lustre which may be called metallic; but its particles cohere together very feebly, and it has not been procured in a state capable of conducting electricity. These points, however, require further investigation before a decisive opinion on the subject can be adopted. (Pog. Annalen, iv.)

Oxide of Zirconium was discovered in the year 1789 by Klaproth in the Jargon or Zircon of Ceylon, and has since been found in the Hyacinth from Expailly in France. Berthier prepares it by fusing zircon in fine powder with litharge in the ratio of 17 to 21, when a glass is obtained which is soluble in acids. It is an earthy substance, resembling alumina in appearance, of sp. gr. 4·3, having neither taste nor odour, and quite insoluble in water. It is so hard that it will scratch glass. Its colour, when pure, is white; but it has frequently a tinge of yellow, owing to the presence of iron, from which it is separated with great difficulty. It phosphoresces vividly when heated strongly before the blowpipe. Its salts are distinguished from those of alumina or glucina by being precipitated by all the pure alkalies, in an excess of which it is insoluble. The alkaline carbonates precipitate it as carbonate of zirconia, and a small portion of it is redissolved by an excess of the precipitant, especially when a bicarbonate is employed. It differs from all the earths, except thorina, in being precipitated when any of its neutral salts are boiled with a saturated solution of sulphate of potassa, the zirconia subsiding as a subsalt, and the potassa remaining in solution as a bisulphate. Zirconia is precipitated from its salts by pure ammonia as a bulky hydrate, which is readily soluble in acids; but if this hydrate is ignited, dried, or even washed with boiling water, it afterwards resists the action of the acids, and is dissolved by them with great difficulty. Strong sulphuric acid is then its best solvent (Berzelius). When hydrated zirconia is heated to commencing redness, it parts with its water, and soon after emits a very vivid glow for a short time. This phenomenon appears to depend upon the particles of the zirconia suddenly approaching each other, and thus acquiring much greater density than it previously possessed. Oxide of chromium, titanic acid, and several other compounds afford instances of the same appearance; and whenever it takes place, the susceptibility of the substance to be attacked by fluid reagents is greatly diminished (Berzelius).

The composition of zirconia has not yet been satisfactorily determined. From some analyses by Berzelius, described in the Essay above referred to, it is probable that the eq. of this earth is about 33·7; its symb. $2Zr + 3O$, $\underline{\dddot{Zr}}$, or $Zr_2 O_3$.

Sulphuret of Zirconium.—This compound may be prepared, according to Berzelius, by heating zirconium with sulphur in an atmosphere of hydrogen gas; and the union is effected with feeble emission of light. The product is pulverulent, a non-conductor of electricity, of a dark chestnut-brown colour, and without lustre. It is insoluble in sulphuric, nitric, and hydrochloric acid; and it is slowly attacked by nitro-hydrochloric acid, even with the aid of heat. It is readily dissolved by hydrofluoric acid, with disengagement of hydrogen gas.

CLASS II.

METALS, THE OXIDES OF WHICH ARE NEITHER ALKALIES NOR EARTHS.

ORDER I.

METALS WHICH DECOMPOSE WATER AT A RED HEAT.

SECTION X.

MANGANESE.

Hist. and Prep.—The black oxide of manganese was described in the year 1774 by Scheele as a peculiar earth, and Gahn subsequently showed that it contains a new metal, to which he gave the name of *magnesium;* a term since applied to the metallic base of magnesia, and for which the words *manganesium* and *manganium* have been substituted. This metal, owing doubtless to its strong affinity for oxygen, has never been found in an uncombined state in the earth; but its oxides are very abundant. The metal may be obtained by forming finely powdered oxide of manganese into a paste with oil, laying the mass in a hessian crucible lined with charcoal, luting down a cover carefully, and exposing it during an hour and a half, or two hours, to the strongest heat of a smith's forge.

Prop.—A hard brittle metal, of a greyish-white colour, and granular texture. Its sp. gr. according to John, is 8·013. When pure it is not attracted by the magnet, but Berthier has lately stated that it possesses this property at very low temperatures. It is exceedingly infusible, requiring the highest heat of a wind furnace for fusion. It soon tarnishes on exposure to the air, and absorbs oxygen with rapidity when heated to redness in open vessels. It slowly decomposes water at common temperatures with disengagement of hydrogen gas; but at a red heat decomposition is rapid, and protoxide of manganese is generated. Decomposition of water is likewise occasioned by dilute sulphuric acid, and sulphate of protoxide of manganese is the product.

Berzelius, from an analysis of chloride of manganese, found 27·7 as the eq. of manganese, a number which agrees closely with my own experiments on the same chloride. Its symb. is Mn. The composition of the compounds of manganese described in this section is as follows:—

	Manganese.			Equiv.	Formulæ.
Protoxide	27·7	1 eq.+Oxygen	8	1 eq.= 35·7	$Mn+O$.
Sesquioxide	55·4	2 eq.+do.	24	3 eq.= 79·4	$2Mn+3O$.
Peroxide	27·7	1 eq.+do.	16	2 eq.= 43·7	$Mn+2O$.
Red Oxide	83·1	3 eq.+do.	32	4 eq.=115·1	$3Mn+4O$.
Varvicite	110·8	4 eq.+do.	56	7 eq.=166·8	$4Mn+7O$.
Manganic Acid	27·7	1 eq.+do.	24	3 eq.= 51·7	$Mn+3O$.
Permang. Acid	55·4	2 eq.+do.	56	7 eq.=111·4	$2Mn+7O$.
Protochloride	27·7	1 eq.+Chlor.	35·42	1 eq.= 63·12	$Mn+Cl$.
Perchloride	55·4	2 eq.+do.	247·94	7 eq.=303·34	$2Mn+7Cl$.
Perfluoride	55·4	2 eq.+Fluor.	130·76	7 eq.=186·16	$2Mn+7F$.
Protosulphuret	27·7	1 eq.+Sulphur.	16·1	1 eq.= 43·8	$Mn+S$.

OXIDES OF MANGANESE.

In studying metallic oxides, it is necessary to distinguish oxides formed by the direct union of oxygen and a metal, from those that consist of two other oxides united with each other, and which therefore, in composition, partake of the nature of a salt rather than of an oxide. An instance of this kind of combination is supplied by the black oxide of iron; and it is probable that two of the five compounds enumerated as oxides of manganese have a similar constitution. Their composition has been particularly investigated by Berzelius, Thomson (First Principles, i.), Arfwedson,[*] Berthier,[†] and myself.[‡]

Protoxide.—Prep.—By this term is meant that oxide of manganese which is a strong salifiable base, is contained in all the ordinary salts of this metal, and which appears to be its lowest degree of oxidation. This oxide may be formed by exposing the peroxide, sesquioxide, or red oxide of manganese, to the combined agency of charcoal and a white heat; or by exposing either of the oxides of manganese contained in a tube of glass, porcelain, or iron, to a current of hydrogen gas at an elevated temperature. The best material for this purpose is the red oxide prepared from nitrate of oxide of manganese; since the native oxides, especially the peroxide, are fully reduced to the state of protoxide by hydrogen with difficulty. The reduction commences at a low red heat; but to decompose all the red oxide, a full red heat is required. The same compound is formed by the action of hydrogen gas at an intense white heat. Wöhler and Liebig have shown that the protoxide is also obtained by fusing chloride of manganese in a platinum crucible with about twice its weight of carbonate of soda, and its own weight of sal-ammoniac, and afterwards dissolving the chloride of sodium by water.

---

[*] Letter from Berzelius in the An. de Ch. et Ph. vi.

[†] Ibid. xx.

[‡] Philos. Trans. of Edin. for 1828; or Phil. Mag. and Annals, iv.

Prop.—Protoxide of manganese, when pure, is of a light green colour, very near the mountain green. According to Forchammer it attracts oxygen rapidly from the air; but in my experiments it was very permanent, undergoing no change either in weight or appearance during the space of nineteen days. At 600° it is oxidized with considerable rapidity, and at a low red heat is converted in an instant into red oxide. It sometimes takes fire when thus heated, especially when the mass is considerable. It unites readily with acids without effervescence, producing the same salts as when the same acids act on carbonate of oxide of manganese. When it comes in contact with concentrated sulphuric acid, intense heat is instantly evolved; and the same phenomenon is produced, though in a less degree, by strong hydrochloric acid. The resulting salt is the same as when these acids are heated with either of the other oxides of manganese. If quite pure, the protoxide should readily and completely dissolve in cold dilute sulphuric acid, and yield a colourless solution.

In order to prepare a pure salt of manganese from the common peroxide of commerce, the following process may be employed:—The solution which remains when chlorine is made by the action of muriatic acid on peroxide of manganese is rendered neutral by gently evaporating it to dryness. A portion, which varies with the proportion of iron present, and is easily ascertained by trial on a small scale, is then precipitated by an excess of carbonate of soda, and the mixed precipitate of carbonate of manganese and peroxide of iron, well washed, is digested with the remainder of the liquid. The protoxide of manganese enters the liquid, expelling the peroxide of iron, and at last a liquid is obtained quite free from iron. It ought to give a bright flesh-coloured precipitate with hydrosulphuret of ammonia, and a white with ferrocyanide of potassium. Should the first drop of the former test cause a dark precipitate, this is owing to the presence, not of iron, but of cobalt and nickel, which, according to Gregory, are almost uniformily present in small quantity in the oxide of manganese. They are easily removed by adding the hydrosulphuret till it gives a pure flesh-coloured precipitate. If the oxide, before being dissolved in muriatic acid, has been digested in very diluted muriatic acid, and washed, no lime can be present in the solution. The iron can only escape complete precipitation if it be partly in the state of protoxide; but in preparing chlorine the iron is fully oxidized. If, however, protoxide should be present, it is readily peroxidized by boiling with a little nitric acid. This process, suggested by Everitt, is founded on the fact, that all carbonates of protoxides, when digested with solutions of peroxide of iron, precipitate the latter; and the manganese contained in the mixed solution is thus ingeniously made use of to effect its own purification. (Phil. Mag. and An. vi. 193.) Other less convenient methods, which, however, yield a pure product, have been suggested, particularly one by Faraday. (Quart. Journ. vi.)

The salts of manganese are in general colourless if quite pure; but more frequently they have a shade of pink, owing to the presence of a little red oxide or permanganic acid. The protoxide is precipitated from its solutions as a white hydrate of ammonia, or the pure fixed alkalies; as white carbonate of protoxide of manganese by alkaline carbonates and bicarbonates; and as white ferrocyanuret of manganese by ferrocyanuret of potassium, a character by which the absence of iron may be demonstrated. These white precipitates, with the exception of that obtained by means of a bicarbonate, very soon become brown from the absorption of oxygen. None of the salts of manganese which contain a strong acid, such as the nitric, or sulphuric, are precipitated by hydrosulphuric acid. With an alkaline hydrosulphate, on the contrary, a flesh-coloured precipitate is formed, which is a hydrated protosulphuret of manganese: when heated in close vessels, it yields a dark-coloured sulphuret, and water is evolved.

Its eq. is 35·7; symb. $\mathrm{Mn} + \mathrm{O}$, $\dot{\mathrm{M}}\mathrm{n}$, or MO.

Sesquioxide.—Hist. and Prep.—This oxide occurs nearly pure in nature, and as a hydrate it is found abundantly, often in large prismatic crystals, at Jhlefeld in the Hartz. It may be formed artificially by exposing peroxide of manganese for a considerable time to a moderate red heat, and therefore is the chief residue of the usual process for procuring a supply of oxygen gas; but it is difficult so to regulate the degree and duration of the heat, that the resulting oxide shall be quite pure.

Prop.—The colour of the sesquioxide of manganese varies with the source from which it is derived. That which is procured by means of heat from the native peroxide or hydrated sesquioxide, has a brown tint; but when prepared from nitrate of oxide of manganese, it is nearly as black as the peroxide, and the native sesquioxide is of the same colour. With sulphuric and hydrochloric acids it gives rise to the same phenomenon as the peroxide, but of course yields a smaller proportional quantity of oxygen and chlorine gases. It is more easily attacked than the peroxide by cold sulphuric acid. With strong nitric acid it yields a soluble protonitrate and the peroxide, and when boiled with dilute sulphuric acid, it undergoes a similar change. From the proportion of oxygen and manganese in this oxide, it has sometimes been regarded as a compound of 43·7 parts or 1 eq. of peroxide, and 35·7 parts or 1 eq. of protoxide of manganese. In that case the sesquioxide would be constituted like a salt, and should have the properties of that class of compounds; but Mitscherlich has succeeded in combining it with sulphuric acid, and has obtained with it an alum similar in form and constitution to those of peroxide of iron and alumina. It must therefore be considered as a direct compound of 2 eq. of manganese and 3 eq. of oxygen.

Its eq. is 79·4; symb. $2M + 3O$, $\dddot{M}$, or M_2O_3.

Peroxide.—Hist. and Prep.—The well-known ore commonly called, from its colour, black oxide of manganese. It generally occurs massive, of an earthy appearance, and mixed with other substances, such as siliceous and aluminous earths, oxide of iron, and carbonate of lime. It is sometimes found, on the contrary, in the form of minute prisms grouped together, and radiating from a common centre. In these states it is anhydrous; but the essential ingredient of one variety of the earthy mineral called *wad* is hydrated peroxide of manganese, consisting of 1 eq. of water and 2 of the oxide. The peroxide may be made artificially by exposing nitrate of oxide of manganese to a commencing red heat, until the whole of the nitric acid is expelled; but I have never succeeded in procuring it quite pure by this process, because the heat required to drive off the last traces of acid likewise expels some oxygen from the peroxide. The hydrated peroxide, containing 1 eq. of water and 1 of oxide, is formed by precipitating the protochloride of manganese by chloride of lime; and the same compound results from the decomposition of the acids of manganese, either in water or by dilute acid.

Prop.—Not changed by exposure to the air, is insoluble in water, and does not unite either with acids or alkalies. When boiled with sulphuric acid, it yields oxygen gas, and a sulphate of the protoxide is formed. With hydrochloric acid, chloride of manganese is generated, and chlorine is evolved. The solution in both cases is of a deep-red colour, provided undissolved oxide is present; but if separated from the undissolved portions, it is readily rendered colourless by heat. The colour is commonly attributed to a small quantity of the sesquioxide or red oxide of manganese dissolved by the free acid; but Mr. Pearsall, of Hull, has gone far to prove that it is owing to the presence of permanganic acid. (R. Inst. Journal, N. S. No. iv. 49.) The action of sulphuric acid in the cold is exceedingly tardy and feeble, a minute quantity of oxygen gas is slowly disengaged, and the acid acquires an amethyst-red tint. On exposure to a red heat, it is converted, with evolution of oxygen gas, into the sesquioxide of manganese.

Peroxide of manganese is employed in the arts, in the manufacture of glass, and in preparing chlorine for bleaching. In the laboratory it is used for procuring chlorine and oxygen gases, and in the preparation of the salts of manganese.

Red Oxide.—The substance called red oxide of manganese, *Oxidum Manganoso-Manganicum* of Arfwedson, occurs as a natural production, and may be formed artificially by exposing the peroxide of sesquioxide to a white heat either in close or open vessels. It is also produced by absorption of oxygen from the atmosphere when the protoxide is precipitated from its salts by pure alkalies, or when the anhydrous protoxide or carbonate is heated to redness. It is very permanent in the air, not passing to a higher stage of oxidation at any temperature. Its colour when rubbed to the same degree of fineness is brownish-red when cold, and nearly black while warm. Fused with borax or glass it communicates a beautiful violet tint, a character by which manganese may be easily detected before the blowpipe; and it is the cause of the rich colour of the amethyst. It is acted on by strong sulphuric and hydrochloric acids, with the aid of heat, in the same manner as the peroxide and sesquioxide, but of course yields proportionally a smaller quantity of oxygen and chlorine gases. By cold concentrated sulphuric acid it is dissolved in small quantity, without appreciable disengagement of oxygen gas, and the solution is promoted by a slight increase of temperature. The liquid has an amethyst tint, which disappears when heat is applied, or by the action of deoxidizing substances, such as protochloride of tin, or sulphurous and phosphorous acids, sulphate of protoxide of manganese being generated. By strong nitric acid, or when boiled with dilute sulphuric acid, it undergoes the same kind of change as the sesquioxide.

It may be doubted whether the red oxide is not rather a kind of salt composed of two other oxides, than a direct compound of manganese and oxygen. From the ratio of its elements it may consist either of

Sesquioxide .	79·4 or 1 equiv.	or	Peroxide .	43·7 or 1 equiv.
Protoxide .	35·7 or 1 equiv.		Protoxide .	71·4 or 2 equiv.
	115·1			115·1

It contains 27·586 per cent. of oxygen, and loses 6·896 per cent. when converted into the green oxide. Its eq. is 115·1; its symb. either $MnO + Mn_2O_3$, or $2MnO + MnO_2$.

Varvicite.—This compound is known only as a natural production, having been first noticed a few years ago by Mr. Phillips among some ores of manganese found at Hartshill, in Warwickshire. The locality of the mineral suggested its name; but I have also detected it as the constituent of an ore of manganese from Jhlefeld, sent me by Professor Stromeyer. Varvicite was at first mistaken for peroxide of manganese, to which in the colour of its powder it bears considerable resemblance; but it is readily distinguished from that ore by its stronger lustre, greater hardness, more lamellated texture, which is very similar to that of manganite, and by yielding water freely when heated to redness. Its sp. gr. is 4·531. It has not been found regularly crystallized; but my specimen from Jhlefeld is in *pseudo-crystals*, possessing the form of the six-sided pyramid of calcareous spar. When strongly heated it is converted into red oxide, losing 5·725 per cent. of water, and 7·385 of oxygen. It is probably, like the red oxide, a compound of two other oxides; and the proportions just stated justify the supposition that it consists of 2 eq. of peroxide and 1 of sesquioxide of manganese, united in the mineral with an eq. of water. (Phil. Mag. and Annals, v. 209, vi. 281, and vii. 284.)

It has been inferred from some experiments of Berzelius and John, that there are two other oxides of manganese, which contain less oxygen than the green or protoxide. We have no proof, however, of the existence of such compounds.

Its eq. is 166·8; symb. probably $M_2O_3 + 2MO_2$.

Manganic Acid.—Hist. and Prep.—Manganese is one of those metals which is capable of forming an acid with oxygen. Manganate of potassa is generated when hydrate or carbonate of potassa is heated to redness with peroxide of manganese; and nitre may be used successfully, provided the heat be high enough to decompose the nitrite of potassa. The materials absorb oxygen from the air when fused in open vessels; but manganate of potassa is equally well formed in close vessels, one portion of oxide of manganese then supplying oxygen to another. The product has been long known under the name of *mineral chameleon*, from the property of its solution to pass rapidly through several shades of colour: on the first addition of cold water a green solution is formed, which soon becomes blue, purple, and red; and ultimately a brown flocculent matter, hydrated peroxide of manganese, subsides, and the liquid becomes colourless. These changes, which are more rapid by dilution with hot water, have been successively elucidated by Chevillot and Edwards, Forchammer, and Mitscherlich. (An. de Ch. et Ph. viii., and xlix. 113; and An. of Phil. xvi.)

Prop.—The phenomena above mentioned are owing to the formation of manganate of potassa of a green colour, and to its ready conversion into the red permanganate of potassa, the blue and purple tints being due to a mixture of these compounds. Manganic acid itself cannot be obtained in an uncombined state, because it is then resolved into the hydrated peroxide and oxygen, a property which Mitscherlich availed himself of in analyzing this acid; but Mitscherlich has proved that it is analogous in composition to sulphuric acid, and its salts isomorphous with the sulphates. Manganate of potassa is obtained in crystals by forming a concentrated solution of mineral chameleon in cold water, very pure and free from carbonic acid, allowing it to subside in a stoppered bottle, and evaporating the clear green solution in vacuo with the aid of sulphuric acid. All contact of paper and other organic matter must be carefully avoided, since they deoxidize the acid, and the process be conducted in a cool apartment. The crystals are anhydrous, and permanent in the dry state; but in solution the carbonic acid of the air suffices to decompose the acid, or even simple dilution with cold water. Mixed with a solution of potassa the manganate may be crystallized a second time in vacuo without change.

Its eq. is 51·7; symb. $Mn + 3O$, $\dddot{Mn}$, or MnO_3.

Permanganic Acid.—*Prep.*—Permanganate of potassa is obtained by heating a solution of mineral chameleon, however prepared. A better process has been indicated by Wöhler (Pog. An. xxvii. 626): it consists in fusing chlorate of potassa in a platinum crucible, and then adding peroxide of manganese in fine powder. An improvement on this has been proposed by Gregory (Lieb. An. xv: 237): he recommends 4 parts of peroxide of manganese to be mixed in fine powder with 3½ parts of chlorate of potassa, and then added to 5 parts of hydrate of potassa dissolved in a small quantity of water. The whole is evaporated to perfect dryness, powdered, and exposed in a platinum crucible to a low red heat. The mass, which has not been fused, is again powdered, and added to a large quantity of boiling water, which when clear is decanted from the sediment of peroxide of manganese, rapidly concentrated and allowed to crystallize. The crystals are at first small and almost black; but by washing with a little cold water, and resolution in the smallest possible quantity of boiling water, they are obtained in very fine crystals. The acid may be obtained by adding to a solution of permanganate of baryta a quantity of dilute sulphuric acid exactly sufficient for precipitating the baryta.

Prop.—Has a rich red colour; is more stable than the manganic acid, though still very prone to decomposition. Contact with paper or linen as in filtering, particles of cork, organic particles floating in the atmosphere, decompose it rapidly, for which reason Gregory recommends that all solutions containing it should be filtered through a pledget of asbestus, placed in the throat of the funnel. Colouring matters are bleached by it; and in pure water its decomposition begins at 86° and is complete at 212°. On these occasions oxygen gas is abstracted or given out, and hydrated peroxide of manganese subsides. Its salts are more permanent than the free acid, so that most of them may be boiled in solution, especially if concentrated. When heated they give out oxygen gas, and are reconverted into manganates. They deflagrate like nitre with burning charcoal, and detonate powerfully with phosphorus. Their colour in solution is a rich purple, and a small quantity of the salt imparts this colour to a very large quantity of water. When mixed with dilute nitric acid and boiled, oxygen gas is evolved, and hydrated peroxide of manganese subsides, from the respective quantities of which Mitscherlich ascertained the composition of the acid. In addition to the remarkable analogy which its constitution bears to perchloric acid, Mitscherlich finds that permanganate and perchlorate of potassa are isomorphous, an observation confirmed by Miller.

Its eq. is 111·4; symb. $2\,Mn + 7O$, $\overset{\cdot\cdot\cdot\cdot\cdot\cdot\cdot}{\underline{Mn}}$, or Mn_2O_7.

Protochloride of Manganese.—This compound is best prepared by evaporating a solution of the chloride to dryness by a gentle heat, and heating the residue to redness in a glass tube, while a current of hydrochloric acid gas is transmitted through it. The heat of a spirit-lamp is sufficient for the purpose. It fuses readily at a red heat, and forms a pink-coloured lamellated mass on cooling. It is deliquescent, and of course very soluble in water.

Its eq. is 63·12; symb. $Mn + Cl$, or $MnCl$.

Perchloride of Manganese.—Hist. and Prep.—Dumas discovered this compound, which is readily formed by putting a solution of permanganic into strong sulphuric acid, and then adding fused sea-salt. The hydrochloric and permanganic acids mutually decompose each other; water and perchloride of manganese are generated, and the latter escapes in the form of vapour. The best mode of preparation is to form the green mineral chameleon, and acidulate with sulphuric acid: the solution, when evaporated, leaves a residue of sulphate and permanganate of potassa. This mixture, treated by strong sulphuric acid, yields a solution of permanganic acid, into which are added small fragments of sea-salt, as long as coloured vapour continues to be evolved. (Edin. Journ. of Science, viii. 179.)

Prop.—The perchloride, when first formed, appears as a vapour of a copper or greenish colour; but on traversing a glass tube cooled to -4°, it is condensed into a greenish-brown coloured liquid. When generated in a capacious tube, its vapour gradually displaces the air, and soon fills the tube. If it is then poured into a large flask, the sides of which are moist, the colour of the vapour changes instantly on coming into contact with the moisture, a dense smoke of a pretty rose-tint appears, and hydrochloric and permanganic acids are generated. It is hence analogous in composition to permanganic acid, its elements being in such a ratio that

$$\underset{Mn_2Cl_7}{\text{1 eq. perchloride}} \text{ and } \underset{7HO}{\text{7 eq. water}} \text{ yield } \underset{Mn_2O_7}{\text{1 eq. permang. acid}} \text{ and } \underset{7HCl.}{\text{7 eq. hydrochloric acid}}$$

Hence its eq. is 303·34; symb. $2Mn + 7Cl$, or Mn_2Cl_7.

Perfluoride of Manganese.—This gaseous compound, discovered by Dumas and Wöhler (Edin. Journ. of Science, ix.), is best formed by mixing common mineral chameleon with half its weight of fluor-spar, and decomposing the mixture in a platinum vessel by fuming sulphuric acid. The fluoride is then disengaged in the form of a greenish-yellow gas or vapour, of a more intensely yellow tint than chlorine. When mixed with atmospheric air, it instantly acquires a beautiful purple-red colour; and it is freely absorbed by water, yielding a solution of the same red tint. It acts instantly on glass, with formation of fluosilicic acid gas, a brown matter being at the same time deposited, which becomes of a deep purple-red tint on the addition of water.

It may be inferred from the experiments of Wöhler that this yellow gas is a fluoride of manganese; that when mixed with water both compounds are decomposed, and hydrofluoric and permanganic acids generated, which are dissolved; that a similar formation of the two acids ensues from the admixture of the yellow gas with atmospheric air, owing to the moisture contained in the latter; and that by contact with glass, fluosilicic acid gas is produced, and anhydrous permanganic acid deposited. In consequence of its acting so powerfully on glass, its other properties have not been ascertained; but from those above mentioned, its composition is obviously similar to that of the gaseous chloride of manganese.

Its eq. is 186·16; symb. $2Mn + 7F$, or Mn_2F_7.

The *protosulphuret* of *manganese* may be procured by igniting the sulphate with one-sixth of its weight of charcoal in powder. (Berthier.) It is also formed by the action of hydrosulphuric acid gas on the protosulphate at a red heat. (Arfwedson in An. of Phil. vol. vii. N.S.) It occurs native in Cornwall and at Nagyag in Transylvania. It dissolves completely in dilute sulphuric or hydrochloric acid, with disengagement of very pure hydrosulphuric acid gas. Its eq. is 43·8; symb. $Mn + S$, or MnS.

SECTION XI.

IRON.

Hist.—KNOWN from the remotest antiquity. The occurrence of native iron, except that of meteoric origin, which always contains nickel and cobalt, is exceedingly rare; and few of the specimens said to be such have been well attested. In combination, however, especially with oxygen and sulphur, it is abundant; being contained in animals and plants, and being diffused so universally in the earth, that there are few mineral substances in which its presence may not be detected. Minerals which contain iron in such form, and in such quantity, as to be employed in the preparation of the metal, are called *ores of iron;* and of these the principal are the following. The red oxides of iron included under the name of red hæmatite; the brown hæmatite of mineralogists, consisting of hydrated peroxide of iron; the black oxide, or magnetic iron ore;

and carbonate of protoxide of iron, either pure, or in the form of clay iron ore, when it is mixed with siliceous, aluminous, and other foreign substances. The three former occur most abundantly in primary districts, and supply the finest kinds of iron, as those of Sweden and India; while clay-iron stone, from which most of the English iron is extracted, occurs in secondary deposites, and chiefly in the coal formation.

Prep.—The extraction of iron from its ores is effected by exposing the ore, previously roasted and reduced to a coarse powder, to the action of charcoal, or coke, and lime at a high temperature. The action of carbonaceous matter in depriving the ore of its oxygen is obvious; and the lime plays a part equally important. It acts as a flux by combining with all the impurities of the ore, and forming a fusible compound called a *slag*. The whole mass being thus in a fused state, the particles of reduced metal descend by reason of their greater density, and collect at the bottom; while the slag forms a stratum above, protecting the melted metal from the action of the air. The latter, as it collects, runs out at an aperture in the side of the furnace; and the fused iron is let off by a hole in the bottom, which was previously filled with sand. The process is never successful unless the flux, together with the impurities of the ore, are in such proportion as to constitute a fusible compound. The mode of accomplishing this object is learned only by experience; and as different ores commonly differ in the nature or quantity of their impurities, the workman is obliged to vary his flux according to the composition of the ore with which he operates. Thus if the ore is deficient in siliceous matter, sand must be added; and if it contain a large quantity of lime, proportionally less of that earth will be required. Much is often accomplished by the admixture of different ores with each other. The slag consists of a compound of earthy salts, similar to some siliceous minerals, in which silicic acid is combined with lime, alumina, magnesia, protoxide of manganese, and sometimes oxide of iron. The most usual combination, according to Mitscherlich, is bisilicate of lime and magnesia, sometimes with a little protoxide of iron; a compound which he has obtained in crystals, having the precise form and composition of Augite. Artificial minerals may in fact by such processes be procured, similar in form and composition to those which occur in the earth. We are indebted to Mitscherlich for some valuable facts on this subject (An. de Ch. et Ph. xxiv. 355).

The iron obtained by this process is the cast iron of commerce, and contains a considerable quantity of carbon, unreduced ore, and earthy substances. It is converted into soft or malleable iron by exposure to a strong heat while a current of air plays upon its surface. By this means any undecomposed ore is reduced, earthy impurities rise to the surface as slag, and carbonaceous matter is burned. The exposed iron is also more or less oxidized at its surface, and the resulting oxide, being stirred with the fused metal below, facilitates the oxidation of the carbon. As the purity of the iron increases, its fusibility diminishes, until at length, though the temperature continue the same, the iron becomes solid. It is then subjected, while still hot, to the operation of rolling or hammering, by which its particles are approximated, and its tenacity greatly increased. It is then the malleable iron of commerce. It is not, however, absolutely pure; for Berzelius has detected in it about one-half per cent. of carbon, and it likewises contains traces of silicon. The carbonaceous matter may be removed by mixing iron filings with a quarter of its weight of black oxide of iron, and fusing the mixture, confined in a covered hessian crucible, by means of a blast furnace. A little powdered green glass should be laid on the mixture, in order that the iron may be completely protected from the air by a covering of melted glass, and any unreduced oxide dissolved. But the best and readiest mode of procuring iron in a state of perfect purity, is by transmitting hydrogen gas over the pure oxide heated to redness in a tube of porcelain. The oxygen of the oxide unites with hydrogen, and the metal is left in the form of a porous spongy mass.

Prop.—Iron has a peculiar grey colour, and strong metallic lustre, which is susceptible of being heightened by polishing. In ductility and malleability it is inferior to several metals, but exceeds them all in tenacity. At common temperatures it is very hard and unyielding, and its hardness may be increased by being heated and then suddenly cooled; but it is at the same time rendered brittle. When heated to redness it is remarkably soft and pliable, so that it may be beaten into any form, or be intimately incorporated or *welded* with another piece of red-hot iron by hammering. Its texture is fibrous. Its sp. gr. may be estimated at 7·7; but it varies slightly according to the degree with which it has been rolled, hammered, or drawn, and it is increased by fusion. In its pure state it is exceedingly infusible, requiring for fusion the highest temperature of a wind furnace. It is attracted by the magnet, and may itself be rendered permanently magnetic by several processes; — a property of great interest and importance, and which is possessed by no other metal excepting nickel. It retains this quality, however, only within certain temperatures: thus iron of an orange-red heat ceases to be attracted, and a steel magnet loses its polarity at the boiling point of almond oil—a loadstone just below visible ignition (Faraday).

Iron, in its ordinary state, has a strong affinity for oxygen. In a perfectly dry atmosphere it undergoes no change; but when moisture is present, its oxidation, or *rusting*, is rapid. In the first part of the change carbonate of protoxide of iron is generated; but the protoxide gradually passes into hydrated peroxide, and the carbonic acid at the same time is evolved. Rust of iron always contains ammonia, a circumstance which indicates that the oxidation is probably accompanied by decomposition of water; and Chevalier has observed that ammonia is also present in the native oxides of iron. Heated to redness in the open air, iron absorbs oxygen rapidly, and is converted into black scales, called the *black oxide* of iron; and in an atmosphere of oxygen gas it burns with vivid scintillations. The same effect was observed by Bierley on exposing a bar of iron at a full white heat to the blast of a powerful pair of bellows. This has been confirmed by D'Arcet, who also obtained the combustion by causing the heated iron to revolve rapidly through the air: for this purpose he attached one extremity of the bar by means of wire to a string, and then whirled it rapidly round. Magnus has observed that the spongy mass obtained by reducing the oxide of iron with hydrogen may be obtained at a heat considerably below that of redness; and that when the iron, thus reduced, is exposed to the air, it takes fire spontaneously, and the oxide is instantly reproduced. This singular property, which Magnus has also remarked in nickel and cobalt prepared in a similar manner, appears to depend on the extremely divided and expanded state of the metallic mass; for when the reduction is effected at a red heat, which enables the metal to acquire its natural degree of compactness, the phenomenon is not observed. If the oxide be mixed with a little alumina, and then reduced at a red heat, the presence of the earth prevents that contraction which would otherwise ensue: the metal is in the same mechanical condition as when it is deoxidized at a low temperature, and its spontaneous combustibility is preserved.

Iron decomposes the vapour of water, by uniting with its oxygen, at all temperatures, from a dull red to a white heat ; a singular fact when it is considered, that at the very same temperatures the oxides of iron are reduced to the metallic state by hydrogen gas. (Gay-Lussac in An. de Ch. et de Physique, i. 36.) These opposite effects, various instances of which are known to chemists, are accounted for by a mode of reasoning similar to that explained on a former occasion (page 150). It is rapidly oxidized by sulphuric and nitric acids : in the former case the oxidation occurs at the sole expense of water, the hydrogen of which is at the same time evolved, while in the latter the nitric acid itself yields a part of its oxygen. The action of nitric acid on iron is attended by a series of very remarkable phenomena, which have recently been observed by Professor Schönbein. He first observed that nitric acid, of sp. gr. 1·35, though capable of acting with great violence on ordinary iron, was perfectly inert on a portion of iron wire one extremity of which had been made red hot previously to its introduction into the acid. He found, too, that this indifference to nitric acid may be communicated by mere contact from one iron wire to another, by submersion for a few moments into strong nitric acid, or by making it the positive electrode of a galvanic current, the negative electrode having been previously introduced into the acid. It is remarkable that under these circumstances the iron wire possesses the properties of one of gold or platinum, and does not combine with the oxygen liberated at its surface. Faraday, who has examined this voltaic condition of iron with his usual success, has remarked that the same property is communicated to iron by contact with platinum, and that the effect is not limited to nitric acid, but extends to various saline solutions which are usually acted on by iron. For the particulars on this interesting subject the reader may consult the original papers of Schönbein and Faraday in the Phil. Mag. and An. ix. 53 ; x. 133, 172, 175, 267, 428.

The equivalent of iron has not yet been determined with accuracy. From the analysis of its oxides by Berzelius, Stromeyer, and Gay-Lussac, it may be estimated at 27·16, 27·8, and 28·3. In the uncertainty as to which of these numbers is the most accurate, I shall continue to use 28, the number generally adopted in this country. Its symb. is Fe. The composition of the compounds of iron described in this section is as follows :—

	Iron.				Equiv.	Formulæ.
Protoxide	28	1 eq.+Oxyg.	8	1 eq.	= 36	Fe+O or FeO.
Peroxide	56	2 eq.+do.	24	3 eq.	= 80	2Fe+3O or Fe_2O_3.

	Iron.				Equiv.	Formulæ.
Black Oxide	Protoxide		36	1 eq.	=116	$FeO+Fe_2O_3$.
	Peroxide		80	1 eq.		
Protochloride	28	1 eq.+Chlor.	35·42	1 eq.	= 63·42	$Fe+Cl$ or $FeCl$.
Perchloride	56	2 eq.+do.	106·26	3 eq.	=162·26	$2F+3Cl$ or Fe_2Cl_3.
Protiodide	28	1 eq.+Iodine	126·3	1 eq.	=154·3	$Fe+I$ or FeI.
Periodide	56	2 eq.+do.	378·9	3 eq.	=434·9	$2Fe+3I$ or F_2I_3.
Protobromide	28	1 eq.+Brom.	78·4	1 eq.	=106·4	$Fe+Br$ or $FeBr$.
Perbromide	56	2 eq.+do.	235·2	3 eq.	=291·2	$2\ Fe+3Br$ or Fe_2Br_3.
Protofluoride	28	1 eq.+Fluor.	18·68	1 eq.	= 46·68	$Fe+F$ or FeF.
Perfluoride	56	2 eq.+Fluor.	56·04	3 eq.	=112·04	$2Fe+3F$ or Fe_2F_3.
Tetrasulphuret	112	4 eq.+Sulph.	16·1	1 eq.	=128·1	$4Fe+S$ or Fe_4S.
Disulphuret	56	2 eq.+do.	16·1	1 eq.	= 72·1	$2Fe+S$ or Fe_2S.
Protosulphuret	28	1 eq.+do.	16·1	1 eq.	= 44·1	$Fe+S$ or FeS.
Sesquisulphuret	56	2 eq.+do.	48·3	3 eq.	=104·3	$2Fe+3S$ or Fe_2S_3.
Bisulphuret	28	1 eq.+do.	32·2	2 eq.	= 60·2	$Fe+2S$ or FeS_2.
Magnetic Pyrites	Bisulph. of iron		60·2	1 eq.	=280·7	$5FeS+FeS_2$.
	Protosulph. of iron		220·5	5 eq.		
Diphosphuret	56	2 eq.+Phosp.	15·7	1 eq.	= 71·7	$2Fe+P$ or Fe_2P.
Perphosphuret	84	3 eq.+do.	62·8	4 eq.	=146·8	$3F+4P$ or Fe_3P_4.
Carburets.	Constitution not determined.					

OXIDES OF IRON.

Protoxide.—This oxide is the base of the native carbonate of iron, and of the green vitriol of commerce. Its existence was inferred some years ago by Gay-Lussac (An. de Ch. vol. lxxx.); but it is doubtful if it has ever been obtained in an insulated form. Its salts, particularly when in solution, absorb oxygen from the atmosphere with such rapidity that they may even be employed in eudiometry. This protoxide is always formed with evolution of hydrogen gas when metallic iron is put into dilute sulphuric acid; and its composition may be determined by collecting and measuring the gas which is disengaged.

Protoxide of iron is precipitated from its salts as a white hydrate by pure alkalies, as a white carbonate by alkaline carbonates, and as a white ferrocyanuret by ferrocyanuret of potassium. The two former precipitates become first green and then red, and the latter green and blue, by exposure to the air. The solution of gall-nuts produces no change of colour. Hydrosulphuric acid does not act if the protoxide is united with any of the stronger acids; but alkaline hydrosulphates cause a black precipitate, protosulphuret of iron.

Its eq. is 36; symb. $Fe + O$, $\dot{Fe}$, or FeO.

Peroxide.—Hist. and Prep.—The red or peroxide is a natural product, known to mineralogists under the name of *red hæmatite.*

It sometimes occurs massive, at other times fibrous, and occasionally in the form of beautiful rhomboidal crystals. It may be made chemically by dissolving iron in nitro-hydrochloric acid, and adding an alkali. The hydrate of the red oxide of a brownish-red colour subsides, which is identical in composition with the mineral called *brown hæmatite*, and consists of 80 parts or 1 eq. of the peroxide, and 18 parts or 2 eq. of water.

Prop.—Is not attracted by the magnet. Fused with vitreous substances it communicates to them a red or yellow colour. It combines with most of the acids, forming salts, the greater number of which are red. Its presence may be detected by very decisive tests. The pure alkalies, fixed or volatile, precipitate it as the hydrate. Alkaline carbonates have a similar effect, peroxide of iron not forming a permanent salt with carbonic acid. With ferrocyanuret of potassium it forms Prussian blue. Sulphocyanuret of potassium causes a deep blood-red, and infusion of gall-nuts a black colour. Hydrosulphuric acid converts the peroxide into protoxide of iron, with deposition of sulphur. These reagents, and especially ferrocyanuret and sulphocyanuret of potassium, afford an unerring test of the presence of minute quantities of peroxide of iron. On this account it is customary, in testing for iron, to convert it into the peroxide, an object which is easily accomplished by boiling the solution with a small quantity of nitric acid.

Its eq. is 80; symb. $2Fe + 3O$, $\underline{\dddot{Fe}}$, or Fe_2O_3.

Black or Magnetic Oxide.—*Hist. and Prep.*—This substance, the *oxidum ferroso-ferricum* of Berzelius, long supposed to be protoxide of iron, contains more oxygen than the protoxide, and less than the red oxide. It cannot be regarded as a definite compound of iron and oxygen; but it is composed of the two real oxides. It occurs native, frequently crystallized in the form of a regular octohedron and dodecahedron; and it is not only attracted by the magnet, but is itself sometimes magnetic. It is always formed when iron is heated to redness in the open air; and is likewise generated by the contact of watery vapour with iron at elevated temperatures. The composition of the product, however, varies with the duration of the process and the temperature which is employed. Thus, according to Bucholz, Berzelius, and Thomson, 100 parts of iron, when oxidized by steam, unite with nearly 30 of oxygen; whereas in a similar experiment performed by Gay-Lussac, 37·8 parts of oxygen were absorbed. The oxide of Gay-Lussac has the composition stated in the table; and Berzelius thinks that of magnetic iron ore to be similar. This has been satisfactorily confirmed by Abich, by precipitating a mixture of the two oxides from their solution in sulphuric acid, in which they were contained in their equivalent proportions. The green precipitate which falls he found to be as highly magnetic as the native magnetic iron ore, and to suffer no change on exposure to the atmosphere. But if the protoxide were contained in the solution in greater quantity, its presence in the precipitate as such was indicated by the production of the hydrated peroxide on exposure to the air. An excess of the peroxide diminished the magnetic effects. (An. de Ch. et Ph. lx. 369.) Gregory has observed, that when a solution of protosulphate of iron is divided into two equal parts, one of which is peroxidized, then mixed with the other, and precipitated by ammonia at a boiling heat, a black oxide is obtained, which does not attract oxygen in drying, and is highly magnetic. Its composition must be $2FeO + Fe_2O_3$; as the two solutions contain equal quantities of iron; and Gregory suggests that it may occur native as a variety of magnetic iron ore. Wöhler (Liebig's Annalen, xxii. 56) erroneously gives the above proportions for forming the common magnetic oxide, $FeO, + Fe_2O_3$; to obtain which 1 part of protosulphate should be mixed with 2 of the same salt peroxidized by nitric acid. M. Mosander states, that on heating a bar of iron in the open air, the outer layer of the scales contains a greater quantity of peroxide than the inner layer. The former consists of 1 eq. of peroxide to 4 of the protoxide, and in the latter are contained 1 eq. of peroxide to 6 eq. of protoxide. The inner layer seems uniform in composition; but the outer is variable, its more exposed parts being richer in oxygen.

The nature of the black oxide is farther elucidated by the action of acids. On digesting the black oxide in sulphuric acid, an olive-coloured solution is formed, containing two salts, sulphate of the peroxide and protoxide, which may be separated from each other by means of alcohol. (Proust and Gay-Lussac.) The solution of these mixed salts gives green precipitates with alkalies, and a very deep blue ink with infusion of gall-nuts. The black oxide of iron is the cause of the dull green colour of bottle glass.

Its eq. is 116; symb. $FeO + Fe_2O_3$.

Protochloride of Iron.—Prep.—This compound is formed by transmitting dry hydrochloric acid gas over iron at a red heat, when hydrogen gas is evolved, and the surface of the iron is covered with a white crystalline protochloride, which at a stronger heat is sublimed. Also, on acting with hydrochloric acid on iron, which is dissolved with evolution of hydrogen gas, evaporating to dryness, and heating to redness in a tube without exposure to the air, a grey crystalline protochloride is left; but it contains some protoxide formed by an interchange of elements between the last portions of water and the chloride, hydrochloric acid being also generated.

Prop.—It dissolves freely in water, yielding a pale green solution, from which rhomboidal prisms of the same colour are obtained by evaporation. The crystals contain several equivalents of water of crystallization, deliquesce by exposure to the air, owing to the formation of perchloride, and are soluble in alcohol as well as water. The aqueous solution absorbs oxygen from the air, and becomes yellow from the formation of perchloride of iron: one portion of iron takes oxygen from the air, and yields its chlorine to another portion of iron, whereby perchloride and peroxide of iron are generated, and the latter falls as an ochreous sediment combined with some of the perchloride. A solution of the protochloride of iron dissolves binoxide of nitrogen with the same phenomena as the protosulphate, a circumstance favourable to the view entertained by many that protochloride of iron is converted by water into hydrochlorate of the protoxide.

Its eq. is 63·42; symb. $Fe + Cl$, or $FeCl$.

Perchloride of Iron.—It is formed by the combustion of iron wire in dry chlorine gas, and by transmitting that gas over iron moderately heated, when it is obtained in small iridescent plates of a red colour, which are volatile at a heat a little above 212°, deliquesce readily, and dissolve in water, alcohol, and ether. On agitating ether with a strong aqueous solution of the perchloride, the ether abstracts a part of it, and acquires a gold-yellow colour. The readiest mode of obtaining a solution of the perchloride is to dissolve peroxide of iron in hydrochloric acid. On concentrating to the consistence of syrup and cooling, it separates as red crystals, which by distillation yield at first water and hydrochloric acid, and then anhydrous perchloride of iron, leaving a compound of peroxide and perchloride of iron in crystalline laminæ. The formation of peroxide appears due to an interchange of elements between it and water. The same kind of interchange ensues between the vapours of water and the perchloride at a high temperature; and this is probably the source, as Mitscherlich suggests, of the crystals of peroxide of iron found in volcanic products.

Its eq. is 162·26; symb. $2Fe + 3Cl$, or Fe_2Cl_3.

Protiodide of Iron.—It exists as a pale green solution when iodine is digested with water and iron wire, the latter being in excess; and on evaporating the solution, without exposure to the air, to dryness and heating moderately, the protiodide is fused, and on cooling becomes an opaque crystalline mass of an iron-grey colour and metallic lustre. It is deliquescent and very soluble in water and alcohol. Its aqueous solution attracts oxygen rapidly from the air, undergoing the same kind of change as the protochloride: to preserve a solution of protiodide as such a long piece of iron wire should be kept permanently in the liquid. This compound has been very successfully employed in medical practice by my colleague Dr. A. T. Thomson.

Its eq. is 154·3; symb. $Fe + I$, or FeI.

The *periodide*, of a yellow or orange colour according to the strength of the solution, is obtained by freely exposing a solution of the protiodide to the air, or digesting iron wire with excess of iodine, gently evaporating, and subliming the periodide. It is a volatile red compound, deliquescent, and soluble in water and alcohol. Its eq. is 434·9; symb. $2Fe + 3I$, or Fe_2I_3.

The *bromides* of iron are formed under similar conditions to the chlorides and iodides, and are very analogous to them in their properties.

Protofluoride of Iron is best prepared by dissolving iron in a solution of hydrofluoric acid, out of which it crystallizes as the acid becomes saturated, in small white square tables, which are sparingly soluble in water, and become pale yellow by the action of the air. By heat they part with their water of crystallization, and afterwards bear a red heat without decomposition. (Berzelius.)

Its eq. is 46·68; symb. $Fe + F$, or FeF.

The *perfluoride* is formed by dissolving peroxide of iron in hydrofluoric acid, and yields a colourless solution even when saturated. By evaporation it is left as a crystalline mass of a pale flesh-colour, and of a mild astringent taste. It is sparingly soluble in water. Its eq. is 112·04; symb. $2Fe + 3F$, or Fe_2F_3.

Sulphurets of Iron.—These elements have for each other a remarkably strong affinity, and unite under various circumstances and in several proportions. The two lowest degrees of sulphuration, the *tetrasulphuret* and *disulphuret*, were prepared by Arfwedson by transmitting a current of hydrogen gas at a red heat over the anhydrous disulphate of peroxide of iron to procure the tetrasulphuret, and over anhydrous sulphate of protoxide of iron for the disulphuret. In both cases sulphurous acid and water are evolved, and the resulting sulphurets are left as greyish black powders susceptible of a metallic lustre by friction. They both dissolve in dilute sulphuric acid with evolution of hydrogen and hydrosulphuric acid gases.

Protosulphuret of Iron is prepared by heating thin laminæ of iron to redness with sulphur in a covered hessian crucible, and continuing the heat until any excess of sulphur is expelled. The iron is found with a crust of protosulphuret, which is brittle, of a yellowish-grey colour and metallic lustre, and is attracted by the magnet. When pure it is completely dissolved by dilute sulphuric acid, yielding pure hydrosulphuric acid. The protosulphuret of iron exists in nature as an ingredient in variegated copper pyrites; and it falls on mixing hydrosulphate of ammonia with sulphate of protoxide of iron as a black precipitate, which oxidizes rapidly by absorbing oxygen from the air as soon as the excess of hydrosulphate of ammonia is removed by washing.

Its eq. is 44·1; symb. $Fe + S$, or FeS.

The *sesquisulphuret* is formed in the moist way by adding perchloride of iron drop by drop to hydrosulphate of ammonia or sulphuret of potassium in excess, and falls as a black precipitate, which is oxidized readily by the air. In the dry way it is slowly produced by the action of hydrosulphuric acid gas on peroxide of iron at a heat not exceeding 212°, water being also formed; and by the action of the same gas on the hydrated peroxide at common temperatures. This sulphuret, when anhydrous, has a yellowish grey colour, is not attracted by the magnet, and dissolves in dilute sulphuric or hydrochloric acid, yielding hydrosulphuric acid and a residue of bisulphuret of iron (Berzelius).

Its eq. is 104·3; symb. $2Fe + 3S$, or Fe_2S_3.

Bisulphuret of iron, *iron pyrites* of mineralogists, exists abundantly in the earth. It occurs in cubes or some allied form, has a yellow colour, metallic lustre, a density of 4·981, and is so hard that it strikes fire with steel. Some varieties have a white colour; but these usually contain arsenic. Others occur in rounded nodules, have a radiated structure divergent from a common centre, are often found in beds of clay, and are much disposed by the influence of air and moisture to yield sulphate of oxide of iron: these are suspected by Berzelius to be compounds of protosulphuret and bisulphuret of iron.

Bisulphuret of iron is not attacked by any of the acids except the nitric, and its best solvent is the nitro-hydrochloric acid. Heated in close vessels it gives off nearly half its sulphur, and is converted into magnetic iron pyrites. By heat and air together it yields peroxide of iron. Its eq. is 60·2; symb. $Fe + 2S$, or FS_2.

Magnetic iron pyrites.—This is a natural product, termed magnetic pyrites, from being attracted by the magnet, and was formerly regarded as protosulphuret of iron; but Stromeyer has shown that its elements are in such a ratio, that it may be regarded as a compound of bisulphuret and protosulphuret. It is formed by heating the bisulphuret to redness in close vessels, by fusing iron filings with half their weight of sulphur, or by rubbing sulphur upon a rod of iron heated to whiteness. It is soluble in dilute sulphuric acid, yielding hydrosulphuric acid gas and a residue of sulphur. It is much more oxidable by air and moisture than the pure bisulphuret. Its eq. is 280·7; symb. $5FeS + FeS_5$.

Diphosphuret of Iron.—It is prepared by exposing the phosphate of protoxide of iron to a strong heat in a covered crucible lined with charcoal, the excess of phosphorus being dissipated in vapour. It is a fused granular mass, of the colour and lustre of iron, but very brittle, and is not attacked by hydrochloric acid. It is sometimes contained in metallic iron, to the properties of which it is very injurious by rendering it brittle at common temperatures. Its eq. is 71·7; symb. $2Fe + P$, or Fe_2P.

The *perphosphuret* has been obtained by Rose by the action of phosphuretted hydrogen gas on sulphuret of iron at a moderate temperature, and resembles the former in its properties.

Its eq. is 146·8; symb. $3Fe + 4P$, or Fe_3P_4.

Carburets of Iron. — Carbon and iron unite in very various proportions; but there are three compounds very distinct from each other—namely, graphite, cast or pig iron, and steel.

Graphite, also known under the names of *plumbago* and *black lead*, occurs not unfrequently as a mineral production, and is found in great purity at Borrowdale in Cumberland. It may be made artificially by exposing iron with excess of charcoal to a violent and long-continued heat; and it is commonly generated in small quantity during the preparation of cast iron. Pure specimens contain about four or five per cent. of iron, but sometimes its quantity amounts to 10 per cent. Most chemists believe the iron to be chemically united with the charcoal; but according to the researches of Karsten of Berlin, native graphite is only a mechanical mixture of charcoal and iron, while artificial graphite is a real carburet.

Graphite is exceedingly unchangeable in the air, and, like charcoal, is attacked with difficulty by chemical reagents. It may be heated to any extent in close vessels without change; but if exposed at the same time to the air, its carbon is entirely consumed, and oxide of iron remains. It has an iron grey colour, metallic lustre, and granular texture; and it is soft and unctuous to the touch. Its chief use is in the manufacture of pencils and crucibles, and in burnishing iron to protect it from rust.

Cast iron is the product of the process for extracting iron from its ores, and is commonly regarded as a real compound of iron and charcoal. It always contains impurities, such as charcoal, undecomposed ore, and earthy matters, which are often visible by mere inspection; and sometimes traces of chromium, manganese, sulphur, phosphorus, and arsenic are present. It fuses readily at 278·6° (Daniell), which is a full red heat, and in cooling it acquires a crystalline granular texture. The quality of different specimens is by no means uniform; and two kinds, white and grey cast iron, are in particular distinguished from each other. The former is exceedingly hard and brittle, sometimes breaking like glass from sudden change of temperature; while the latter is softer and much more tenacious. This difference appears owing to the mode of combination, rather than to a difference in the proportion of carbon; for the white variety may be converted into the grey by exposure to a strong heat and cooling slowly, and the grey may be changed into the white by being heated and rapidly cooled. According to Karsten the carbon of the latter is combined with the whole mass of iron, and amounts as a maximum to 5·25 per cent.; but in some specimens its proportion is considerably less. The former, on the contrary, contains from 3·15 to 4·65 per cent. of carbon, of which about three-fourths are in the state of graphite, and are left as such after the iron is dissolved by acids; while the remaining fourth is in combination with the whole mass of metal, constituting a carburet which is very similar to steel. Grey cast iron may hence be regarded as a kind of steel, in which graphite is mechanically mixed.

Steel is commonly prepared in this country by the process of cementation, which consists in filling a large furnace with alternate strata of bars of the purest malleable iron and powdered charcoal, closing every aperture so as perfectly to exclude atmospheric air, and keeping the whole during several days at a red heat. By this treatment the iron gradually combines with from 1·3 to 1·75 per cent. of carbon, its texture is greatly changed, and its surface is blistered. It is subsequently hammered at a red heat into small bars, and may be welded either with other bars of steel or with malleable iron. Mackintosh, of Glasgow, has introduced an elegant process of forming steel by exposing heated iron to a current of coal gas, when carburetted hydrogen is decomposed, its carbon enters into combination with iron, and hydrogen gas is evolved.

In ductility and malleability it is far inferior to iron; but exceeds it greatly in hardness, sonorousness, and elasticity. Its texture is also more compact, and it is susceptible of a higher polish. It sustains a full red heat without fusing, and is therefore less fusible than cast iron; but it is much more so than malleable iron. By fusion it forms cast steel, which is more uniform in composition and texture, and possesses a closer grain, than ordinary steel.

SECTION XII.

ZINC.—CADMIUM.

ZINC.

Hist. and Prep.—This metal was first mentioned under the term *zinetum* in the sixteenth century by Paracelsus; but it was probably known at a much earlier period. In commerce it is often called, *spelter*, and is obtained either from *calamine*, native carbonate of zinc, or from the native sulphuret, *zinc blende* of mineralogists. It is procured from the former by heat and carbonaceous matters; and from the latter by a similar process after the ore has been previously oxidized by *roasting*, that is, by exposure to the air at a low red heat. Its preparation affords an instance of what is called *distillation by descent.* The furnace or crucible for reducing the ore is closed above, and in its bottom is fixed an iron tube, the upper aperture of which is in the interior of the crucible, and its lower terminates just above a vessel of water. The vapour of zinc, together with all the gaseous products, passes through this tube, and the zinc is condensed. The first portions are commonly very impure, containing cadmium and arsenic, the period of their disengagement being indicated by what the workmen call the *brown blaze;* but when the *blue blaze* begins, that is, when the metallic vapour burns with a bluish white flame, the zinc is collected. As thus obtained, it is never quite pure: it frequently contains traces of charcoal, sulphur, cadmium, arsenic, lead, and copper; and iron is always present. It may be freed from these impurities by distillation,—by exposing it to a white heat in an earthen retort, to which a receiver full of water is adapted; but the first portions, as liable to contain arsenic and cadmium, should be rejected.

Prop.—It has a strong metallic lustre, and a bluish white colour. Its texture is lamellated, and its sp. gr. about 7. It is a hard metal, being acted on by the file with difficulty. At low or high degrees of heat it is brittle; but at temperatures between 210° and 300°, it is both malleable and ductile, a property which enables zinc to be rolled or hammered into sheets of considerable thinness. Its malleability is considerably diminished by the impurities which the zinc of commerce contains. It fuses at 773° (Daniell), and when slowly cooled crystallizes in four or six-sided prisms. Exposed in close vessels to a white heat, it sublimes unchanged.

Zinc undergoes little change by the action of air and moisture. When fused in open vessels it absorbs oxygen, and forms the white oxide, called flowers of zinc. Heated to full redness in a covered crucible, it bursts into flame as soon as the cover is removed, and burns with a brilliant white light. The combustion ensues with such violence, that the oxide as it is formed is mechanically carried up into the air. The heat at which it begins to burn is estimated by Daniell at 941° F. Zinc is readily oxidized by dilute sulphuric or hydrochloric acid, and the hydrogen which is evolved contains a small quantity of metallic zinc in combination.

Gay-Lussac and Berzelius found that the protoxide of zinc consists of 100 parts of metallic zinc and 24·8 of oxygen, being a ratio of 32·3 to 8. Its other combinations justify the adoption of 32·3 as the eq. of zinc; its symb. is Zn. The composition of its compounds described in this section is as follows:—

	Zinc.			Equiv.	Formulæ.
Protoxide .	32·3	1 eq.+Oxygen	8	1 eq.= 40·3	$\mathrm{Zn+O}$ or ZnO.
Peroxide .	Composition uncertain.				
Chloride .	32·3	1 eq.+Chlorine	35·42	1 eq.= 67·72	$\mathrm{Zn+Cl}$ or ZnCl.
Iodide .	32·3	1 eq.+Iodine	126·3	1 eq.=158·6	$\mathrm{Zn+I}$ or ZnI.
Bromine .	32·3	1 eq.+Bromine	78·4	1 eq.=110·7	$\mathrm{Zn+Br}$ or ZnBr.
Fluoride .	32·3	1 eq.+Fluorine	18·68	1 eq.= 50·98	$\mathrm{Zn+F}$ or ZnF.
Sulphuret .	32·3	1 eq.+Sulphur	16·1	1 eq.= 48·4	$\mathrm{Zn+S}$ or ZnS.

Protoxide of Zinc.—This is the only oxide of zinc which acts as a salifiable base, and the only one of known composition. It is generated during the solution of zinc in dilute sulphuric acid, and may be obtained in a dry state by collecting the flakes which rise during the combustion of zinc, or by heating the carbonate to redness. At common temperatures it is white; but when heated to low redness, it assumes a yellow colour, which gradually disappears on cooling. It is quite fixed in the fire. It is insoluble in water, and therefore does not affect the blue colour of plants; but it is a strong salifiable base, forming regular salts with acids, most of which are colourless. It combines also with some of the alkalies.

The presence of zinc is easily recognized by the following characters:—The oxide is precipitated from its solutions as a white hydrate by pure potassa or ammonia, and as carbonate by carbonate of ammonia, but is completely redissolved by an excess of the precipitant. The fixed alkaline carbonates precipitate it permanently as white carbonate of oxide of zinc. Hydrosulphate of ammonia causes a white precipitate, a hydrated sulphuret of zinc. Hydrosulphuric acid acts in a similar manner, if the solution is quite neutral; but it has no effect if an excess of any strong acid is present.

Its eq. is 40·3; symb. $Zn + O$, $\dot{Zn}$, or ZnO.

When metallic zinc is exposed for some time to air and moisture, or is kept under water, it acquires a superficial coating of a grey matter, which Berzelius describes as a sub-oxide. It is probably a mixture of metallic zinc and the white oxide, into which it is resolved by the action of acids. The peroxide is prepared, according to Thenard, by acting on hydrated white oxide of zinc with peroxide of hydrogen diluted with water. It resolves itself so readily into oxygen and the oxide already described, that it cannot be preserved even under the surface of water; and its composition is quite unknown.

Chloride of Zinc.—This compound is formed, with evolution of heat and light, when zinc filings are introduced into chlorine gas; and it is readily prepared by dissolving zinc in hydrochloric acid, evaporating to dryness, and heating the residue in a tube through which dry hydrochloric acid gas is transmitted. It is colourless, fusible at a heat a little above 212°, has a soft consistence at common temperatures, hence called *butter of zinc*, sublimes at a red heat, and deliquesces in the air.

Its eq. is 67·72; symb. $Zn + Cl$, or $ZnCl$.

Iodide of Zinc is prepared by digesting iodine in water with zinc filings in excess. A colourless solution results, which by evaporation yields a deliquescent iodide. By heat in close vessels it may be sublimed, and then crystallizes in brilliant needles; but if heated in the open air, oxide of zinc is formed, and iodine expelled. If zinc is digested in water with an excess of iodine, a brown solution results, which probably contains a biniodide.

Its eq. is 158·6; symb. $\mathrm{Zn} + \mathrm{I}$, or ZnI.

Bromide of Zinc may be formed by a process similar to that for the iodide, but its properties have not been studied.

Its eq. is 110·7; symb. $\mathrm{Zn} + \mathrm{Br}$, or ZnBr.

Fluoride of Zinc is obtained by acting directly on oxide of zinc with hydrofluoric acid, and is a white compound of sparing solubility.

Its eq. is 50·98; symb. $\mathrm{Zn} + \mathrm{F}$, or ZnF.

Sulphuret of Zinc.—This compound is well known to mineralogists under the name of *zinc blende*, and occurs in dodecahedral crystals or some allied form. Its structure is lamellated, lustre adamantine, and colour variable, being sometimes yellow, red, brown, or black. It may be formed artificially by igniting in a closed crucible a mixture of oxide of zinc and sulphur, or sulphate of oxide of zinc and charcoal, or by drying the hydrated sulphuret of zinc. Its eq. is 48·4; symb. $\mathrm{Zn} + \mathrm{S}$, or ZnS.

CADMIUM.

Hist—Cadmium, so called (from καδμεια, a term applied to calamine and to the volatile matters which rise from the furnace in preparing brass) because it is associated with zinc, was discovered in the year 1817, by Stromeyer, in an oxide of zinc which had been prepared for medical use; and he has since found it in several of the ores of that metal, especially in a radiated blende from Bohemia, which contains about five per cent. of cadmium. The late Dr. Clarke detected its existence in some of the zinc ores of Derbyshire, and in the common zinc of commerce. Herapath has found it in considerable quantity in the zinc works near Bristol. During the reduction of calamine by coal, the cadmium, which is very volatile, flies off in vapour mixed with soot and some oxide of zinc, and collects in the roof of the vault, just above the tube leading from the crucible. Some portions of this substance yielded from 12 to 20 per cent. of cadmium. (An. of Phil. xiv. and xvii.)

Prep.—The process by which Stromeyer separates cadmium from zinc or other metals is the following. The ore of cadmium is dissolved in dilute sulphuric or hydrochloric acid, and after adding a portion of free acid, a current of hydrosulphuric acid gas is transmitted through the liquid, by which means the cadmium is precipitated as sulphuret, while the zinc continues in solution. The sulphuret of cadmium is then decomposed by nitric acid, and the solution evaporated to dryness. The dry nitrate is dissolved in water, and an excess of carbonate of ammonia added. The white carbonate of oxide of cadmium subsides, which, when heated to redness, yields a pure oxide. By mixing this oxide with charcoal, and exposing the mixture to a red heat, metallic cadmium is sublimed.

A very elegant process for separating zinc from cadmium was proposed by Wollaston. The solution of the mixed metals is put into a platinum capsule, and a piece of metallic zinc is placed in it. If cadmium is present, it is reduced, and adheres so tenaciously to the capsule, that it may be washed with water without danger of being lost. It may then be dissolved either by nitric or dilute hydrochloric acid.

Prop.—Cadmium, in colour and lustre, has a strong resemblance to tin, but is somewhat harder and more tenacious. It is very ductile and malleable. Its sp. gr. is 8·604 before being hammered, and 8·694 afterwards. It melts at about the same temperature as tin, and is nearly as volatile as mercury, condensing like it into globules which have a metallic lustre. Its vapour has no odour. When heated in the open air, it absorbs oxygen, and is converted into an oxide. Cadmium is readily oxidized and dissolved by nitric acid, which is its proper solvent. Sulphuric and hydrochloric acids act upon it less easily, and the oxygen is then derived from water.

The eq. of cadmium, deduced from Stromeyer's analysis of its oxide, is 55·8. Its symb. is Cd. The composition of its compounds described in this section is as follows:—

	Cadmium.				Equiv.	Formulæ.
Oxide of Cadm.	55·8	1 eq.+Oxygen	8	1 eq.=	63·8	$\mathrm{Cd}+\mathrm{O}$ or CdO.
Chloride . .	55·8	1 eq.+Chlorine	35·42	1 eq =	91·22	$\mathrm{Cd}+\mathrm{Cl}$ or CdCl.
Iodide . .	55·8	1 eq.+Iodine	126·3	1 eq.=	182·1	$\mathrm{Cd}+\mathrm{I}$ or CdI.
Sulphuret .	55·8	1 eq.+Sulphur	16·1	1 eq.=	71·9	$\mathrm{Cd}+\mathrm{S}$ or CdS.

Oxide of Cadmium.—This, the only known, oxide of cadmium is prepared by igniting its carbonate, has an orange colour, is fixed in the fire, and is insoluble in water. It has no action on test paper, but is a strong alkaline base, forming neutral salts with acids. It is precipitated as a white hydrate by pure ammonia, but is redissolved by excess of that alkali. It is precipitated permanently by pure potassa or soda as a hydrate, and by all the alkaline carbonates as carbonate of oxide of cadmium.

Its eq. is 63·8; symb. $Cd + O$, $\dot{C}d$, or CdO.

Chloride of Cadmium.—By dissolving oxide of cadmium in hydrochloric acid and concentrating duly, the chloride with water of crystallization crystallizes in transparent four-sided rectangular prisms, which lose their water by heat and even in a dry air, fuse at a heat short of redness, and acquire a lamellated texture in cooling. At a high temperature it is sublimed.

Its eq. is 91·22; symb. $Cd + Cl$, or $CdCl$.

Iodide of Cadmium may be formed in the same manner as iodide of zinc, is soluble in water and alcohol, and crystallizes by evaporation in large, colourless, transparent, hexagonal tables, which do not change in the air, and have a pearly lustre. By heat they lose water, and then fuse. Its eq. is 182·1; symb. $Cd + I$, or CdI.

Sulphuret of Cadmium occurs in mixture or combination in some kinds of zinc blende, and is easily prepared by the action of hydrosulphuric acid on a salt of cadmium. It has a yellowish-orange colour, and is distinguished from the sulphurets of arsenic by being insoluble in pure potassa, and by sustaining a white heat without subliming (Stromeyer).

Its eq. is 71·9; symb. $Cd + S$, or CdS.

SECTION XIII.

TIN.

Hist. and Prep.—Was known to the ancients, who obtained it principally, if not solely, from Cornwall. The tin of commerce is distinguished into two varieties, called *block* and *grain tin*, both of which are procured from the native oxide by means of heat and charcoal. In Cornwall, which has been celebrated for its tin mines during many centuries, the ore is both extracted from veins, and found in the form of rounded grains among beds of rolled materials, which have been deposited by the action of water. These grains, commonly called *stream tin*, contain a very pure oxide, and yield the purest kind of grain tin. An inferior sort is prepared by heating bars of tin, extracted from the common ore, to very near their point of fusion, when the more fusible parts, which are the purest, flow out; and the less fusible portions constitute block tin. The usual impurities are iron, copper, and arsenic.

Prop.—It has a white colour, and a lustre resembling that of silver. The brilliancy of its surface is but very slowly impaired by exposure to the atmosphere, nor is it oxidized even by the combined agency of air and moisture. Its malleability is very considerable; for the thickness of common tin-foil does not exceed 1-1000th of an inch. In ductility and tenacity it is inferior to several metals. It is soft and inelastic, and when bent backwards and forwards emits a peculiar crackling noise. Its sp. gr. is about 7·291. At 442° it fuses, and if exposed at the same time to the air, its surface tarnishes, and a grey powder is formed. When heated to whiteness, it takes fire and burns with a white flame, being converted into peroxide of tin.

The eq. of tin deduced by Berzelius from his analysis of its oxides is 57·9; its symb. is Sn. The composition of the compounds of tin described in this section is as follows:—

	Tin.			Equiv.	Formulæ.
Protoxide	57·9	1 eq.+Oxygen	8	1 eq.= 65·9	$Sn+O$ or SnO.
Sesquioxide	105·8	2 eq.+ . .	24	3 eq.=129·8	$2Sn+3O$ or Sn_2O_3.
Binoxide	57·9	1 eq.+ . .	16	2 eq.= 73·9	$Sn+2O$ or SnO_2.
Protochloride	57·9	1 eq.+Chlorine	35·42	1 eq.= 93·32	$Sn+Cl$ or $SnCl$.
Bichloride	57·9	1 eq.+ . .	70·84	2 eq.=128·74	$Sn+2Cl$ or $SnCl_2$.
Protiodide	57·9	1 eq.+Iodine	126·3	1 eq.=184·2	$Sn+I$ or SnI.
Biniodide	57·9	1 eq.+ . .	252 6	2 eq.=310·5	$Sn+2I$ or SnI_2.
Protosulphuret	57·9	1 eq.+Sulphur	16·1	1 eq.= 74·0	$Sn+S$ or SnS.
Sesquisulph.	115·8	2 eq.+ . .	48·3	3 eq.=164·1	$2Sn+3S$ or Sn_2S_3.
Bisulphuret	57·9	1 eq.+ . .	32·2	2 eq.= 90·1	$Sn+2S$ or SnS_2.
Terphosphuret	57·9	1 eq.+Phosph.	47·1	3 eq.=105·0	$Sn+3P$ or SnP_3.

Protoxide of Tin.—Prep.—When chloride of tin in solution is mixed with an alkaline carbonate, hydrated oxide of tin falls, which may be obtained as such in a dry form by washing with warm water, and drying at a heat not above 196°, with the least possible exposure to the air. The best mode of obtaining the anhydrous oxide is by heating the hydrate to redness in a tube from which air is excluded by a current of carbonic acid gas. The same oxide is formed when tin is kept for some time fused in an open vessel.

Prop.—Its sp. gr. is 6·666. At common temperatures it is permanent in the air; but if touched by a red-hot body it takes fire, and is converted into the peroxide. It is dissolved by the sulphuric and hydrochloric acids, as also by dilute nitric acid; and the pure fixed alkalies likewise dissolve it. From the alkaline solution metallic tin is gradually deposited, and peroxide of tin remains in solution. Its salts are remarkably prone to absorb oxygen, both from the air and from compounds which yield oxygen readily. Thus it converts peroxide of iron into protoxide, and throws down mercury, silver, and platinum in the metallic state from their salts. With a solution of gold it causes a purple precipitate, the *purple of Cassius*, which appears to be a compound of peroxide of tin and protoxide of gold. By this character protoxide of tin is recognised with certainty. It is thrown down by hydrosulphuric acid as black protosulphuret of tin.

Its eq. is 65·9; symb. $Sn + O$, $\dot{Sn}$, or SnO.

Sesquioxide of Tin.—Fuchs has lately succeeded in preparing this oxide by mixing recently precipitated and moist hydrated peroxide of iron with a solution of protochloride of tin as free as possible from hydrochloric acid; when by an interchange of elements

$$\begin{array}{llcll} \text{1 eq. perox. iron \&} & \text{2 eq. chloride of tin} & & \text{1 eq. sesquiox. tin \&} & \text{2 eq. chlo. iron} \\ Fe_2O_3 & 2SnCl & \text{yield} & Sn_2O_3 & 2FeCl. \end{array}$$

The sesquioxide falls as a slimy grey matter, and in general rather yellow from adhering oxide of iron. Berzelius obtained it purer by using a solution made by saturating hydrochloric acid as far as possible with hydrated peroxide of iron. The sesquioxide of tin, while moist, is soluble in hydrochloric acid, and the solution strikes the purple of Cassius with gold; and it is readily soluble in a solution of ammonia, which distinguishes it from the protoxide of tin, just as its action on gold does from the binoxide (Pog. Annalen, xxviii. 443).

Its eq. is 129·8; symb. $2Sn + 3O$, $\dddot{\underline{Sn}}$, or Sn_2O_3.

Peroxide of Tin.—*Prep.*—Most conveniently by the action of nitric acid on metallic tin. The acid in its most concentrated state, does not act easily upon tin; but when a small quantity of water is added, violent effervescence takes place owing to the evolution of nitrous acid and binoxide of nitrogen, and a white powder, the hydrated peroxide, is produced. On edulcorating this substance, and heating it to redness, watery vapour is expelled, and the pure peroxide, of a straw yellow colour, remains. In this process ammonia is generated, a circumstance which proves water as well as nitric acid to be decomposed. Peroxide of tin may likewise be obtained by precipitation from a solution of perchloride of tin by potassa, ammonia, or the alkaline carbonates; but in this case it falls as a very bulky hydrate, different from the other hydrate both in appearance and several of its chemical properties. Thus the latter dissolves readily in sulphuric, nitric, and hydochloric acid, even when diluted; while the former is completely insoluble in the same acids, even when concentrated. It unites, indeed, with hydrochloric acid, and the compound is soluble in pure water.

Prop.—It has very little disposition in any state to unite with acids, and when dissolved by them, is very apt to separate itself spontaneously as a gelatinous hydrate. It acts the part of a feeble acid: it reddens litmus when its hydrate moistened is laid upon it, and it unites with the pure alkalies, forming soluble compounds which are called *stannates.*

Peroxide of tin is recognized by its insolubility in acids in its anhydrous state; by separating from its solution by means of hydrochloric acid as a bulky hydrate by any of the alkalies or alkaline carbonates, which is easily and completely dissolved by pure potassa or soda in excess; and by yielding with hydrosulphuric acid the yellow bisulphuret of tin, which is also soluble in pure potassa. Peroxide of tin, when melted with glass, forms a white enamel.

Its eq. 73·9; symb. $Sn + 2O$, $\ddot{Sn}$, or SO_2.

Protochloride of Tin.—This compound is obtained by transmitting hydrochloric acid gas over metallic tin heated in a glass tube, when hydrogen gas is evolved; or by distilling a mixture either of granulated tin with an equal weight of bichloride of mercury, or of an amalgam of tin with calomel, urging the heat till the mercury is expelled. In this state it is a grey solid, of a resinous lustre, which fuses below redness, and at a high temperature sublimes. It is obtained by crystallization from a concentrated solution of the chloride in crystals, which are sometimes in small white needles, and at others in large transparent prisms, and consist of 93·32 parts or 1 eq. of protochloride of tin and 27 parts or 3 eq. of water. On heating these crystals, they not only lose water, but reaction ensues between the elements of water and the chloride, hydrochloric acid gas is evolved, and protoxide of tin remains combined with the chloride. The same kind of compound is formed when a large quantity of the water is poured upon the crystals: the solution contains protochloride of tin and hydrochloric acid, and a white powder subsides which consists of 1 eq. of the protochloride, 1 eq. of protoxide, and 2 eqs. of water (Berzelius).

A solution of protochloride of tin is obtained by heating granulated tin in strong hydrochloric acid as long as hydrogen gas continues to be evolved. This solution is much employed as a deoxidizing agent, being more powerful than the sulphate or nitrate of the protoxide; owing apparently to the tendency of the protochloride of tin to resolve itself into bichloride and metallic tin, the latter taking oxygen or chlorine from any metallic solutions which yield them readily. Its eq. is 93·32; symb. $Sn + Cl$, or $SnCl$.

Bichloride of Tin.—When protochloride of tin is heated in chlorine gas, or on distilling a mixture of 8 parts of granulated tin with 24 of bichloride of mercury, a very volatile, colourless, liquid passes over, which is bichloride of tin. In an open vessel it emits dense white fumes, caused by the moisture of the air, and hence it was formerly called the *fuming liquor* of Libavius, who discovered it. At 248° it boils, and the sp. gr. of its vapour was found by Dumas to be 9·1997. With one-third of its weight of water it forms a solid hydrate, and in a larger quantity of water dissolves.

The solution of bichloride of tin, commonly called *permuriate of tin*, is much used in dyeing, and is prepared by dissolving tin in nitro-hydrochloric acid. The process requires care; for if the action be very rapid, as is sure to happen if strong acid be employed and much tin added at once, the peroxide will be spontaneously deposited as a bulky hydrate, and be subsequently redissolved with great difficulty. But the operation will rarely fail, if the acid is made with two measures of hydrochloric acid, one of nitric acid, and one of water, and if the tin is gradually dissolved, one portion disappearing before another is added. The most certain mode of preparation, however, is to prepare a solution of the protochloride, and convert it into the bichloride either by chlorine, or by gentle heat and nitric acid.

Its. eq. is 128·74; symb. $Sn + 2Cl$, or $SnCl_2$.

Iodides of Tin.—The protiodide is formed by heating granulated tin with about $2\frac{1}{2}$ times its weight of iodine, and is a brownish red, translucid substance, very fusible, volatile at a high temperature, and soluble in water.

Its eq. is 184·2; symb. $Sn + I$, or SnI.

The periodide is prepared by dissolving in hydriodic acid the hydrate of the peroxide precipitated by alkalies from the bichloride. It crystallizes in yellow crystals of a silky lustre, which are resolved by boiling water into hydriodic acid and peroxide of tin.

Its eq. is 310·5; symb. $Sn + 2I$, or SnI_2.

Protosulphuret of Tin.—This compound is prepared by pouring melted tin upon its own weight of sulphur, and stirring rapidly with a stick during the action; as some tin usually escapes the sulphur from the latter being rapidly expelled, the product should be pulverized, mixed with its weight of sulphur, and projected in successive portions into a hot hessian crucible, and then heated to redness. It is a brittle compound, of a bluish grey, nearly black, colour and metallic lustre, which fuses at a red heat, and acquires a lamellated texture in cooling. It is dissolved by hydrochloric acid with evolution of hydrosulphuric acid. The same sulphuret is obtained in the moist way by adding hydrosulphuric acid to a solution of protochloride of tin.

Its eq. is 74·0; symb. $Sn + S$, or SnS.

The *Sesquisulphuret* is formed by mixing the protosulphuret in fine powder with a third of its weight of sulphur, and heating the mixture to low redness until sulphur ceases to escape. Its colour is of a deep greyish yellow, it is reconverted by a strong heat into the protosulphuret, and dissolves in hydrochloric acid gas, yielding hydrosulphuric acid gas and a residue of bisulphuret of tin.

Its eq. is 164·1; symb. $2Sn + 3S$, or Sn_2S_3.

Bisulphuret of Tin, formerly called *mosaic gold*, is prepared by heating in a glass or earthen retort a mixture of 2 parts of peroxide of tin, 2 of sulphur, and 1 part of sal-ammoniac, and maintaining a low red heat until sulphurous acid ceases to be evolved. These materials are sometimes employed without sal-ammoniac, but Berzelius says that the latter is essential for obtaining the bisulphuret. The product, when succesfully prepared, is in crystalline scales, and sometimes even in regular six-sided tables, of a golden yellow colour and metallic lustre. It is soluble in pure potassa and in its carbonate by boiling; but its only solvent among the acids is the nitro-hydrochloric. The bisulphuret is obtained as a bulky hydrate of a dirty yellow colour by the action of hydrosulphuric acid or hydrosulphate of ammonia on bichloride of tin in solution.

Its eq. is 90·1; symb. $Sn + 2S$, or SnS_2.

Terphosphuret of Tin.—Rose formed this compound by acting on a solution of protochloride of tin by phosphuretted hydrogen. It is readily oxidized by the action of the air.

Its eq. is 105·0; symb. $Sn + 3P$, or SnP_3.

SECTION XIV.

COBALT.—NICKEL.

COBALT.

Hist.—This metal is met with in the earth chiefly in combination with arsenic, constituting an ore from which all the cobalt of commerce is derived. It is a constant ingredient of meteoric iron, though in very small quantity. (Stromeyer.) Gregory has detected it also in many specimens of native peroxide of manganese. Its name is derived from the term *Kobold, an evil spirit*, applied to it by the German miners at a time when they were ignorant of its value, and considered it unfavourable to the presence of valuable metals.

Prep.—When native arseniuret of cobalt is broken into small pieces, and exposed in a reverberatory furnace to the united action of heat and air, its elements are oxidized, most of the arsenious acid is expelled in the form of vapour, and an impure oxide of cobalt, called *zaffre*, remains. This is dissolved in hydrochloric acid, and a current of hydrosulphuric acid gas is transmitted through the solution until the arsenious acid is completely separated in the form of orpiment. The filtered liquid is then boiled with a little nitric acid, in order to convert the protoxide into peroxide of iron, and an excess of carbonate of potassa is added. The precipitate consisting of peroxide of iron and carbonate of protoxide of cobalt, after being well washed with water, is digested in a solution of oxalic acid, which dissolves the oxide of iron and leaves the oxide of cobalt in the form of an insoluble oxalate. (Laugier.) On heating this oxalate in a retort from which atmospheric air is excluded, a large quantity of carbonic acid is evolved, and a black powder, metallic cobalt, is left. (Thomson in Annals of Philosophy, N. S. i.) The pure metal is easily procured also by passing a current of dry hydrogen gas over oxide of cobalt heated to redness in a tube of porcelain. In this state it is porous, and if formed at a low temperature it inflames spontaneously, as stated in the section on iron.

Prop.—A brittle metal, of a reddish-grey colour, and weak metallic lustre. Its density, according to my observation, is 7·834. It fuses at a heat rather lower than iron, and when slowly cooled it crystallizes. It has long been considered to be attracted by the magnet, but Faraday denies that it possesses this property when pure. It undergoes little change in the air, but absorbs oxygen when heated in open vessels. It is attacked with difficulty by sulphuric or hydrochloric acid, but is readily oxidized by means of nitric acid. Like iron and the other metals of this order, it decomposes water at a red heat with disengagement of hydrogen gas. (Despretz.)

According to the analyses by Rothoff of the oxides of cobalt, its equivalent is inferred to be 29·5 (An. of Phil. iii. 356). Its symb. is Co. The composition of its compounds described in this section is as follows:—

	Cobalt.			Equiv.	Formulæ.
Protoxide .	29·5	1 eq.+Oxygen	8	1 eq.= 37·5	$Co+O$ or CoO.
$\frac{4}{3}$ Oxide .	88·5	3 eq.+ . .	32	4 eq.=120·5	$3Co+4O$ or Co_3O_4.
Peroxide .	59·0	2 eq.+ . .	24	3 eq.= 83·0	$2Co+3O$ or Co_2O_3.
Chloride .	29·5	1 eq.+Chlorine	35·42	1 eq.= 64·92	$Co+Cl$ or $CoCl$.
Protosulphuret	29·5	1 eq.+Sulphur	16·1	1 eq.= 45·6	$Co+S$ or CoS.
Sesquisulphuret	59	2 eq.+ . .	48·3	3 eq.=107·3	$2Co+3S$ or Co_2S_3.
Bisulphuret .	29·5	1 eq.+ . .	32·2	2 eq.= 61·7	$Co+2S$ or CoS_2.
Subphosphuret	88·5	3 eq.+Phosph.	31·4	2 eq.=119·9	$3Co+2P$ or Co_3P_2.

Protoxide of Cobalt.—Prepared by decomposing carbonate of the protoxide by heat in a vessel from which atmospheric air is excluded. It is of an ash-grey colour, and is the basis of the salts of cobalt, most of which are of a pink hue. When heated to redness in open vessels it absorbs oxygen, and is converted into the peroxide. It is easily recognised by giving a blue tint to borax when melted with it; and is employed in the arts, in the form of smalt, for communicating a similar colour to glass, earthenware, and porcelain. It is precipitated from its salts by pure potassa as a blue hydrate, which absorbs oxygen from the air, and gradually acquires a dirty green tint. Pure ammonia likewise causes a blue precipitate, which is redissolved by the alkali if in excess. It is thrown down as a pale pink carbonate by carbonate of potassa, soda, or ammonia; but an excess of the last redissolves it with facility. Hydrosulphuric acid produces no change, unless the solution is quite neutral, or the oxide is combined with a weak acid. Alkaline hydrosulphates always precipitate it as black protosulphuret of cobalt. Its eq. is 37·5; symb. $Co+O$, $\dot{Co}$, or CoO.

$\frac{4}{3}$ *Oxide of Cobalt.*—It is said that when protoxide of cobalt, or the nitrate, carbonate, or oxalate of that oxide, is gently ignited in an open fire, peroxide of cobalt results; but M. Hess has lately shown that the oxide then obtained is analogous in composition to the red oxide of manganese. The peroxide of cobalt is converted into it, with loss of oxygen, by a full red heat, whether exposed to the air or not; so that of the oxides of cobalt it is the most stable. The same compound is obtained as a dirty green hydrate by the action of the air on the hydrated protoxide. It is probably a compound of peroxide and protoxide of cobalt, since $3Co + 4O$ obviously contain the elements $CoO + Co_2O_3$. This intermediate oxide is of a dark brown colour, and does not unite with acids or alkalies (Pog. Annalen, xxvi. 542).

Its eq. is 120·5; symb. $CoO + Co_2O_3$.

Peroxide.—Is obtained as a black hydrate containing 2 eq. of water, $Co_2O_3 + 2HO$, when chloride of cobalt in solution is decomposed by hypochlorite of lime, or chlorine is transmitted into water in which hydrated protoxide of cobalt is suspended. In this case

3 eq. Protoxide &	1 eq. Chlorine		1 eq. Peroxide &	1 eq. Chloride
3 CoO	Cl	yield	Co_2O_3	CoCl.

This hydrate has a black colour and yields the black anhydrous peroxide by exposure to a heat of 600° or 700°; but it is difficult to drive off all the water, without also losing oxygen. It combines with none of the acids, and when digested with hydrochloric acid it emits chlorine gas, and chloride of cobalt is generated.

Its eq. is 83·0; symb. $2Co + 3O$, $\underline{\dddot{Co}}$, or Co_2O_3.

When a salt of cobalt is treated with pure ammonia in close vessels, part of the cobalt is dissolved, and part subsides in form of a blue powder. On admitting atmospheric air, this substance passes to a higher state of oxidation, and is gradually dissolved. If nitrate of cobalt is used, a double salt may be obtained in crystals, which L. Gmelin, to whom we are indebted for these remarks, believes to consist of nitrate and *cobaltate* of ammonia. Of the existence of this acid, however, Winkelblech, who has examined the subject, could obtain no evidence (Lieb. An. xiii. 253).

Chloride of Cobalt.—It is obtained in solution on dissolving metallic cobalt, its protoxide or either of the other oxides in hydrochloric acid, with evolution of hydrogen gas with the first and of chlorine with the latter. It yields a pink-coloured solution, and by evaporation small crystals of the same colour containing water of crystallization. When deprived of water its colour is blue, a character on which is founded its use as a sympathetic ink: when letters are written with a dilute solution of the chloride, the colour is so pale that it is invisible in the cold; but on heating gently the letters appear of a blue colour, and disappear as soon as the chloride has recovered its moisture from the atmosphere. When iron or nickel is present the dry chloride of cobalt is green instead of blue.

Its eq. is 64·92; symb. $Co + Cl$, or $CoCl$.

Sulphurets.—Cobalt appears to unite with sulphur in three proportions; the first being a protosulphuret, the second a sesquisulphuret, and the third a bisulphuret. The protosulphuret may be formed in the dry way either by throwing fragments of sulphur on red-hot cobalt, or by igniting protoxide of cobalt with sulphur; and it is thrown down as a black precipitate from the salts of cobalt by alkaline hydrosulphates, or even by hydrosulphuric acid gas if the salt is quite neutral, or the oxide united with any of the feebler acids. It has a grey colour, a metallic lustre, and a crystalline texture.

Its eq. 45·6; symb. $Co+S$, or CoS.

Arfwedson has observed that when hydrogen gas is transmitted over sulphate of oxide of cobalt heated to redness, water and sulphurous acid are evolved, and a compound remains, called an *oxysulphuret*, consisting of oxide of cobalt united with sulphuret of cobalt. When this substance is exposed to hydrosulphuric acid gas at a red heat, the oxide is decomposed, and the sesquisulphuret is formed.

Its eq. is 107·3; symb. $2Co + 3S$, or Co_2S_3.

The bisulphuret is prepared, according to Setterberg, by heating 2 parts of carbonate of oxide of cobalt intimately mixed with 3 parts of sulphur. The process is conducted in a glass retort, and the heat continued as long as sulphur is expelled; but the temperature should not be suffered to reach that of redness.

Its eq. 61·7; symb. $Co + 2S$, or CoS_2.

Subphosphuret of Cobalt.—Rose obtained this phosphuret by the action of hydrogen gas on subphosphate of oxide of cobalt heated in a tube, water being also generated. In this case

1 eq. Phosphate and	8 eq. Hydrogen	yield	1 eq. Phosphuret and	8 eq. water
$3(Co+O)+(2P+5O)$	$8H$		$3Co+2P$	$8(H+O)$.

This phosphuret is pulverulent and of a grey colour, and is also obtained by the action of phosphuretted hydrogen gas on chloride of cobalt.

Its eq. is 119·9; symb. $3Co+2P$, or Co_3P_2.

NICKEL.

Hist. and Prep.—Nickel is a constituent of meteoric iron, and, according to Gregory, of native peroxide of manganese; but its principal ore is the copper-coloured mineral of Westphalia, termed *kupfernickel*, *copper-nickel; nickel* being an epithet of detraction, applied by the older German miners, because the mineral looked like an ore of copper, and yet they could extract none from it. The preparations of nickel may either be prepared from copper-nickel, which is an arseniuret of nickel containing small quantities of sulphur, copper, cobalt, and iron, or from the artificial arseniuret called *speiss*, a metallurgic production obtained in forming smalt from the roasted ores of cobalt. Various processes have been devised for procuring a pure salt of nickel, but the following appears to me as simple and perhaps as successful as any. After reducing speiss to fine powder, it is digested in sulphuric acid, to which a fourth part of nitric acid is added; and when the solution is saturated with nickel, it is set aside for several hours in order that arsenious acid may separate, and is then filtered. The clear liquid is subsequently mixed with a solution of sulphate of potassa, and set aside to crystallize spontaneously; when a double salt, sulphate of oxide of nickel and potassa, is deposited. Thomson, who proposed this process, states that the crystals thus obtained are quite free from arsenic and iron, and contain no impurities except copper and cobalt. The former is precipitated as sulphuret by a current of hydrosulphuric acid gas, a little free sulphuric acid being previously added; and at the same time any traces of arsenic, if present, would likewise subside as orpiment. The filtered liquid is then heated to expel free hydrosulphuric acid, and the oxides of nickel and cobalt precipitated by carbonate of potassa. The separation of these oxides may then be effected by the method suggested by Berthier; namely, by precipitating them together by pure potassa, and, after washing the mixed hydrates, suspending them in water through which chlorine gas is transmitted to saturation. All the cobalt and generally some nickel is converted into peroxide and thus rendered insoluble; while the greater part of the nickel is dissolved in the form of chloride, and may be removed from the insoluble peroxides by filtration. The metal may be prepared either by heating the oxalate in close vessels, or by the combined action of heat and charcoal or hydrogen on oxide of nickel.

Prop.—It is of a white colour, intermediate between that of tin and silver. It has a strong metallic lustre, and is both ductile and malleable. It is attracted by the magnet, and like iron may be rendered magnetic at common temperatures, but loses this power at 630° (Faraday). Its sp. gr. after fusion is about 8·279, and is increased to near 9·0 by hammering.

Nickel is very infusible, but less so than pure iron. It suffers no change at common temperatures by exposure to air and moisture; but it absorbs oxygen at a red heat, though not rapidly, and is partially oxidized. It decomposes water at the same temperature. Hydrochloric and sulphuric acids act upon it with difficulty; but by nitric acid it is readily oxidized, and forms a nitrate of the protoxide of nickel.

From the analyses of the oxides of nickel by Rothoff and Tupputi the eq. of nickel may be estimated at 29·5. Its symb. is Ni. The composition of its compounds described in this section is as follows:—

	Nickel.				Equiv.	Formulæ.
Protoxide	29·5	1 eq.+Oxygen	8	1 eq.=	37·5	$Ni+O$ or NiO.
Peroxide	59·0	2 eq.+do.	24	3 eq.=	83·0	$2Ni+3O$ or Ni_2O_3.
Chloride	29·5	1 eq.+Chlorine	35·42	1 eq.=	64·92	$Ni+Cl$ or $NiCl$.
Disulphuret	59	2 eq.+Sulphur	16·1	1 eq.=	75·1	$2Ni+S$ or Ni_2S.
Protosulphuret	29·5	1 eq.+do.	16·1	1 eq.=	45·6	$Ni+S$ or NiS.
Subphosphuret	88·5	3 eq.+Phosphorus	31·4	2 eq.=	119·9	$3Ni+2P$ or Ni_3P_2.

Protoxide of Nickel.—This oxide may be formed by heating the carbonate, oxalate, or nitrate to redness in an open vessel, and is then of an ash-grey colour; but after exposure to a white heat, its colour is a dull olive-green. It is not reducible by heat unaided by combustibles. It is not attracted by the magnet. It is a strong alkaline base, and nearly all its salts have a green tint. It is precipitated as a hydrate of a pale-green colour by the pure alkalies, but is redissolved by ammonia in excess; as a pale green carbonate by alkaline carbonates, but is dissolved by an excess of carbonate of ammonia; and as a black sulphuret by alkaline hydrosulphates. Hydrosulphuric acid occasions no precipitate, unless the solution is quite neutral, or the oxide combined with a weak acid. Its eq. is 37·5; symb. $Ni + O$, $\dot{Ni}$, or NiO.

Peroxide.—It is formed by transmitting chlorine gas through water in which the hydrate of the protoxide is suspended. It has a black colour, does not unite with acids, is decomposed by a red heat, and with hot hydrochloric acid forms the chloride with disengagement of chlorine gas.

Its eq. is 83·0; symb. $2Ni + 3O$, $\underline{\dddot{Ni}}$, or Ni_2O_3

Thenard succeeded in preparing a peroxide by the action of peroxide of hydrogen on hydrated protoxide of nickel; but it is uncertain whether the composition of this peroxide is identical with that above described, or different. Two sub-oxides have likewise been enumerated; but their existence is exceedingly problematical.

Chloride of Nickel.—This compound is formed by acting with hydrochloric acid on metallic nickel, its protoxide, or peroxide, hydrogen gas being evolved with the former, and chlorine with the latter. It forms an emerald green solution, and by evaporation yields crystals of the same tint, which lose water or deliquesce according as the air is dry or moist. In its anhydrous state it is yellow; but a small admixture with cobalt causes a green tint. At a low red heat it sublimes and condenses in brilliant scales of a gold-yellow colour.

Its eq. is 64·92; symb. $Ni + Cl$, or $NiCl$.

Protosulphuret of nickel is formed by processes similar to those described for preparing protosulphuret of cobalt. The precipitated sulphuret is dark brown or nearly black, and is dissolved by hydrochloric acid with evolution of hydrosulphuric; while that procured in the dry way is of a greyish yellow colour, and requires for solution nitric or nitro-hydrochloric acid. It occurs as a natural production in very delicate acicular crystals, the *haarkies* of the Germans. Its eq. is 45·6; symb. $Ni + S$, or NiS.

Arfwedson obtained the disulphuret by transmitting hydrogen gas over sulphate of oxide of nickel at a red heat. It is of a lighter yellow and more fusible than the other.

Its eq. is 75·1; symb. $2Ni + S$, or Ni_2S.

Subphosphuret of Nickel.—Rose obtained it by the action of hydrogen gas on subphosphate of oxide of nickel, the same change ensuing as with cobalt; and it is generated by the action of phosphuretted hydrogen gas on chloride of nickel. It has a black colour, is insoluble in hydrochloric acid, but dissolves in nitric acid. Heated by the blowpipe it burns with flame.

Its eq. is 119·9; symb. $3\ Ni + 2Ph$, or Ni_3Ph_2.

CLASS II.

ORDER II.

METALS WHICH DO NOT DECOMPOSE WATER AT ANY TEMPERATURE, AND THE OXIDES OF WHICH ARE NOT REDUCED TO THE METALLIC STATE BY THE SOLE ACTION OF HEAT.

SECTION XV.

ARSENIC.

Hist and Prep.—Metallic arsenic sometimes occurs native but more frequently it is found in combination with other metals, and especially with cobalt and iron. On roasting these arsenical ores in a reverberatory furnace, the arsenic, from its volatility, is expelled, combines with oxygen as it rises, and condenses into thick cakes on the roof of the chimney. The sublimed mass, after being purified by a second sublimation, is the virulent poison known by the name of *arsenic* or *white oxide of arsenic.* From this substance the metal itself is procured by heating it with charcoal. The most convenient process is to mix the white oxide with about twice its weight of black flux, and expose the mixture to a red heat in a hessian crucible, over which is luted an empty crucible for receiving the metal. The reduction is easily effected, and metallic arsenic collects in the upper crucible, which should be kept cool for the purpose of condensing the vapour.

Prop.—An exceedingly brittle metal, of a strong metallic lustre, and white colour, running into steel grey. Its structure is crystalline, and when slowly sublimed it is said to crystallize in rhombohedrons. Its sp. gr. is 5·8843. When heated to 356° it sublimes without previously liquefying; for its point of fusion is far above that of its sublimation, and has not hitherto been determined. Its vapour has a strong odour of garlic; a property which affords a distinguishing character for metallic arsenic, as it is not possessed by any other metal, with the exception perhaps of zinc, which is said to emit a similar odour when thrown in powder on burning charcoal, an effect, however, most probably due to the presence of arsenic in the zinc. In close vessels it may be sublimed without change; but if atmospheric air be admitted, it is rapidly converted into the white oxide. According to Hahneman it is slowly oxidized and dissolved by being boiled in water. In general it speedily tarnishes by exposure to air and moisture, acquiring upon its surface a dark film, which is extremely superficial; but Berzelius remarks that he has kept some specimens in open vessels for years without loss of lustre, while others are oxidized through their whole substance, and fall into powder. It has lately been suggested (Liebig's Annalen, 1840), that this effect is owing to the presence of potassium, derived from the black flux. The arsenic sublimed from the cakes which occur in commerce is permanent in the air. The product of this spontaneous oxidation, which is known abroad under the name of *fly-powder*, is supposed by Berzelius to be an oxide; but it is more generally regarded as a mixture of white oxide and metallic arsenic.

The eq. of arsenic, as inferred by Berzelius from the composition of arsenious and arsenic acids, is 37·7. Its symb. is As. The compounds of this metal described in this section are thus constituted:—

	Arsenic.				Equiv.	Formulæ.
Arsenious Acid	75·4	2 eq.+Oxygen	24	3 eq.=	99·4	$2As+3O$ or As_2O_3.
Arsenic Acid	75·4	2 eq.+do.	40	5 eq.=	115·4	$2As+5O$ or As_2O_5.
Protochloride	37·7	1 eq.+Chlorine	35·42	1 eq.=	73·12	$As+Cl$ or $AsCl$.
Sesquichloride	75·4	2 eq.+do.	106·26	3 eq.=	181·66	$2As+3Cl$ or As_2Cl_3.
Periodide	75·4	2 eq.+Iodine	631·5	5 eq.=	706·9	$2As+5I$ or As_2I_5.
Sesquibromide	75·4	2 eq.+Bromine	235·2	3 eq.=	313·6	$2As+3Br$ or As_2Br_3.
Protohyduret	37·7	1 eq.+Hydrogen	1	1 eq.=	38·7	$As+H$ or AsH.
Arseniur. Hydro.	75·4	2 eq.+do	3	3 eq.=	78·4	$2As+3H$ or As_2H_3.
Protosulphuret	37·7	1 eq.+Sulphur	16·1	1 eq.=	53·8	$AS+S$ or AsS.
Sesquisulphuret	75·4	2 eq.+do.	48·3	3 eq.=	123·7	$2As+3S$ or As_2S_3.
Persulphuret	75·4	2 eq.+do.	80·5	5 eq.=	155·9	$2As+5S$ or As_2S_5.

Arsenious Acid.—Prep.—This compound, frequently called *white arsenic* and *white oxide of arsenic*, is always generated when arsenic is heated in open vessels, and may be prepared by digesting the metal in dilute nitric acid. The white arsenic of commerce is derived from the native arseniurets of cobalt, being sublimed during the roasting of these ores for the preparation of zaffre, and it is purified by a second sublimation in iron vessels.

Prop.—It is commonly sold in the state of a fine white powder; but when first sublimed, it is in the form of brittle masses, more or less transparent, colourless, of a vitreous lustre, and conchoidal fracture. This glass, which may also be obtained by fusion, gradually becomes opaque without undergoing any apparent change of constitution, either with respect to water or any other substance;

but the change is certainly promoted by exposure to the atmosphere. Its sp. gr. is 3·7. At 380° it is volatilized, yielding vapours which do not possess the odour of garlic, and which condense unchanged on cold surfaces. Its point of fusion is rather higher than that at which it sublimes; and therefore, in order to be fused, it must either be heated under pressure, or its temperature be suddenly raised above 380°. Arsenious acid is *dimorphous*, that is, susceptible of assuming two crystalline forms belonging to different systems of crystallization. By slow sublimation in a glass tube it is always obtained in distinct octohedral crystals of adamantine lustre and perfectly transparent. Its unusual form is that of six-sided scales derived from a rhombic prism, and was first lately found by Wöhler among the products in a manufacture of smalt: the conditions for enabling it to assume this form are unknown, and by subliming the crystals, they crystallized in octohedrons. (An. de Ch. et Ph. li. 201.)

The taste of arsenious acid is stated differently by different persons. It is prevalently thought to be acrid; but I am satisfied from personal observation that it may be deliberately tasted without exciting more than a very faint impression of sweetness, and perhaps of acidity. The acrid taste ascribed to it has probably been confounded with the local inflammation, by which its application, if of some continuance, is followed. (Christison on Poisons.) It reddens vegetable blue colours feebly, an effect which is best shown by placing the acid in powder on moistened litmus paper. It combines with salifiable bases, forming salts which are termed *arsenites*.

According to the experiments of Klaproth and Bucholz, 1000 parts of boiling water dissolve 77·75 of arsenious acid; and the solution, after having cooled to 60° F., contains only thirty parts. The same quantity of water at 60°, when mixed with the acid in powder, dissolves only two parts and a half.* Guibourt has lately observed that the transparent and opaque varieties of arsenic differ in solubility. He found that 1000 parts of temperate water dissolve, during 36 hours, 9·6 of the transparent, and 12·5 of the opaque variety; that the same quantity of boiling water dissolves 97 parts of the transparent variety, retaining 18 when cold, but takes up 115 of the opaque variety, and retains 29 on cooling. By the presence of organic substances, such as milk or tea, its solubility is materially impaired. (Christison on Poisons.)

When metallic arsenic is sharply heated with hydrate of potassa, pure hydrogen gas is evolved, and a mass is left consisting of arseniuret of potassium and arsenite of potassa; facts, which prove that a portion of arsenic is oxidized, and derives its oxygen partly from water and partly from potassa. If the heat is raised to redness, the arsenious acid is resolved into arsenic acid and metal, the former remaining as an arseniate, while the latter is expelled. Similar phenomena ensue with the hydrates of soda, baryta, and lime; except that with the two latter no arsenic acid is produced. (Soubeiran in An. de Ch. et Ph. xliii. 410.)

Its eq. 99·4; symb. $2As + 3O$, $\overset{\cdots}{\underline{As}}$, or As_2O_3.

The frequent exhibition of arsenious acid as a poison renders the detection of this compound an object of great importance to Medical Practitioners as well as to the Chemist. In this as in all similar inquiries, the object to be held in view is the discovery of a few decisive characters, by means of which the poison may be distinguished from all other bodies, and when present but in small quantity, either in pure water, or in any fluids likely to be met with in the stomach, may with certainty be detected. The attention should be fixed on one or two tests of admitted value, and all others be set aside. With this feeling I shall indicate the mode of applying the four principal tests, namely, the ammoniaco-nitrate of silver, ammoniaco-sulphate of copper, hydrosulphuric acid, and hydrogen gas.

1. Arsenious acid is not precipitated by nitrate of oxide of silver unless an alkali is present, to neutralize the nitric acid. Ammonia is commonly employed for the purpose; but as arsenite of oxide of silver is very soluble in ammonia, an excess of the alkali would retain the arsenite in solution. To remedy this inconvenience, Hume, of Long Acre, proposed to employ the ammoniacal nitrate of silver, which is made by dropping ammonia into a rather strong solution of lunar caustic till the oxide of silver at first thrown down is *nearly* all dissolved. The liquid thus prepared contains the precise quantity of ammonia which is required; and when mixed with arsenious acid, two neutral salts result, the soluble nitrate of ammonia, and the insoluble yellow arsenite of oxide of silver. Ammoniacal nitrate of silver likewise diminishes the risk of fallacy that might arise from the presence of phosphoric acid. Phosphate of oxide of silver is so very soluble in ammonia, that when a neutral phosphate is mixed with the ammoniacal nitrate of silver, the resulting phosphate is held almost entirely in solution by the free ammonia.

This test, however, even in its improved state, is still liable to objection. For when arsenious acid in small proportion is mixed with sea salt, or animal and vegetable infusions, the arsenite of oxide of silver either does not subside at all, or is precipitated in so impure a state that its characteristic colour cannot be distinguished. Several methods have been proposed for obviating this source of fallacy; but Christison has shown, that this test, taken singly, cannot be relied on in practice.

2. Ammoniacal sulphate of copper, which is made by adding ammonia to a solution of sulphate of oxide of copper until the precipitate at first thrown down is nearly all redissolved, occasions with arsenious acid a green precipitate, which has been long used as a pigment under the name of *Scheele's green*. This test, though well adapted for detecting arsenious acid dissolved in pure water, is very fallacious when applied to mixed fluids. Christison has proved that ammoniacal sulphate of copper produces in some animal and vegetable infusions, containing no arsenic, a greenish precipitate, which may be mistaken for Scheele's green; whereas in other mixed fluids, such as tea and porter, to which arsenic has been previously added, it occasions none at all, if the arsenious acid is in small quantity. In some of these liquids, a free vegetable acid is doubtless the solvent; for arsenite of oxide of copper is also dissolved by tannic acid, and perhaps by other vegetable as well as some animal principles.

3. When a current of hydrosulphuric acid gas is conducted through a solution of arsenious acid, the fluid immediately acquires a yellow colour, and in a short time becomes turbid, owing to the formation of orpiment, the sesquisulphuret of arsenic. The precipitate is at first partially suspended in the liquid; but as soon as free hydrosulphuric acid is expelled by heating the solution, it subsides perfectly, and may easily be collected on a filter. One condition, however, must be observed in order to ensure success, namely, that the liquid does not contain a free alkali; for sulphuret of arsenic is dissolved with remarkable facility by pure potassa or ammonia. To avoid this fallacy, it is necessary to acidulate the solution with a little acetic or hydrochloric acid. Hydrosulphuric acid likewise acts on arsenic in all vegetable and animal fluids if previously boiled, filtered, and acidulated.

But it does not necessarily follow, because hydrosulphuric acid causes a yellow precipitate, that arsenic is present; since there are not less than four other substances, namely, selenium, cadmium, tin, and antimony, the sulphurets of which, judging from their colour alone, might possibly be mistaken for orpiment. From these and all other substances whatever, the sulphuret of arsenic may be thus distinguished.—On drying the sulphuret, mixing it with black flux, and heating the mixture contained in a glass tube to redness by means of a spirit-lamp, decomposition ensues, and a metallic crust of an iron-grey colour externally, and crystalline on its inner surface, is deposited on the cool part of the tube. This character alone is quite satisfactory; but it is easy to procure additional evidence, by reconverting the metal into arsenious acid, so as to obtain it in the form of resplendent octohedral crystals. This is done by holding that part of the tube to which the arsenic adheres about three-fourths of an inch above a very small spirit-lamp flame, so that the metal may be slowly sublimed. As it rises in vapour, it combines with oxygen, and is deposited in crystals within the tube. The character of these crystals with respect to volatility, lustre, transparency, and form, is so exceedingly well marked, that a practised eye may safely identify them, though their weight should not exceed the 100th part of a grain. This experiment does not succeed unless the tube be quite clean and dry.

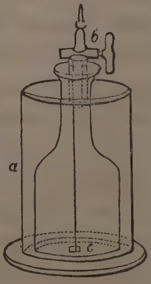
The only circumstance which occasions a difficulty in the preceding process, is the presence of organic substances, which cause the precipitate to subside imperfectly, render filtration tedious, and froth up inconveniently during the reduction. Hence, if so abundant as materially to impede filtration and prevent the liquid from becoming clear, they should be removed before hydrosulphuric acid is employed. This is often sufficiently effected by acidulating with acetic acid, by which caseous and albuminous substances are coagulated; but a more complete separation is accomplished by evaporating the solution at a moderate heat to dryness, redissolving anew by boiling successive portions of distilled water on the residue, and then filtering the solution after it has cooled. Most of the organic matters are thus rendered insoluble. It is of course necessary towards the close of the desiccation to guard against too high a temperature, since otherwise the arsenic itself might be expelled. (Christison on Poisons, 2nd edition, 252.)

The black flux employed in the processes for reducing arsenic, is prepared by deflagrating a mixture of bitratrate of potassa with rather less than half its weight of nitre. The nitric and tartaric acids undergo decomposition, and the solid product is charcoal derived from tartaric acid, and pure carbonate of potassa. As it contains a deliquescent salt, it should be kept in well-stopped bottles.

When this substance is employed in the reduction of arsenious acid or its salts, the charcoal is of course the decomposing agent; but the alkali is of use in retaining the arsenious acid until the temperature is sufficiently high for its decomposition. With sulphuret of arsenic, on the contrary, the alkali is the active principle, the potassium of which unites with sulphur and liberates the arsenic; but the charcoal operates usefully by facilitating the decomposition of the alkaline carbonate. The whole of the arsenic, however, is not sublimed; but part of it enters into union with potassium, and remains with the flux.

4. For the application of hydrogen in testing for arsenic we are indebted to the ingenuity of Marsh (Edinburgh New Phil. Journ. October, 1836). Its employment is dependent on the fact, that whenever hydrogen in the nascent state is brought into contact with any compound of oxygen and arsenic, the latter is instantly decomposed, and water and a gaseous compound of arsenic and hydrogen, the arseniuretted hydrogen, are generated. If the gas be inflamed as it escapes into the air through a fine tube, it burns with the production of the vapour of water, while metallic arsenic or arsenious acid is deposited, according as the supply of oxygen be more or less abundant. Hence if a piece of cold window-glass be held in the flame, its surface is instantly covered with a thin coating of metallic arsenic; but if the flame be made to burn in the centre of a glass tube open at both extremities, the inner surface of the latter is covered in the course of half a minute with arsenious acid. If the tube be held obliquely against it, both depositions take place, and on bringing the tube, while still warm, to the nose a peculiar odour of arsenic is readily perceived.

The experiment is made in the following manner. The suspected substances, if in the solid form, such as bread, must first be boiled with a few ounces of distilled water, and the clear solution while still hot is to be separated from the solid parts by filtration. The same process must be adopted with very thick soups, or the contents of the stomach; while thin soups, wine, beer, coffee, tea, and similar fluids require no previous preparation. The liquid is then mixed with a few ounces of dilute sulphuric acid, and introduced into the apparatus represented by the accompanying woodcut. This consists of two parts, a cylindrical glass vessel *a*, and a capped bell jar



furnished with a stop-cock and small gas-burner; to the stop-cock is suspended a string, to which a fragment of zinc *c*, reaching nearly to the bottom of the bell jar, is attached. The stop-cock *b* being open, when the liquid to be examined is poured into *a* it rises in the bell jar, and so much must be used that the latter is almost full. By the action of the dilute acid on the zinc hydrogen is rapidly evolved, and after permitting a small quantity to escape in order to ensure the removal of atmospheric air from the vessel, the stop-cock is turned, and the gas allowed to accumulate in the bell jar. On burning it the presence of arsenic is readily recognized by the characters above stated, and by the light blue tint it communicates to the flame. The extreme delicacy of this method has been recently amply attested by Liebig and Mohr in their valuable journal (Lieb. Annal. xxiii. 217). To avoid every source of fallacy, however, several precautions are necessary: the most important are—to ensure the perfect purity of the reagents used, as arsenic is commonly contained both in the zinc and sulphuric acid of commerce; to employ a fresh piece of zinc with each experiment, as a portion of the arsenic in the solution is deposited as a metallic crust on the zinc, which is thus rendered impure; and to prove experimentally the purity of the apparatus before each experiment. Liebig recommends that a fragment of porcelain be held in the flame instead of the window-glass, as a very thin film of metallic arsenic is better seen on the white opaque ground than on the transparent glass. He observes, too, that owing to the rapid evolution of the gas, other metals, as for example iron, which may be contained in the solution, being carried up by the hydrogen and deposited on the porcelain, may prove a source of error to the inexperienced. For this reason he recommends that the gas, instead of being burnt by the jet, be transmitted through a fine tube of difficultly fusible glass; on bringing a part of the glass to a red-heat by a spirit-lamp flame, the arseniuretted hydrogen is decomposed as it passes, and the metallic arsenic is deposited just beyond the heated part of the glass, while other metals are deposited in the hot parts themselves.

It was hoped that this test might prove infallible even in the hands of inexperienced chemists; but according to a recent discovery of Mr. L. Thompson, antimony combines with hydrogen, forming with it a gaseous compound which is similar to arseniuretted hydrogen in the mode of its production, in the colour of its flame when burnt, and in the deposition of a metallic crust on a cold surface. The two gases may nevertheless be readily distinguished by decomposing them by means of heat while passing through a fine tube, as was proposed by Liebig for arseniuretted hydrogen; for although the metallic crusts are very similar, yet by attention to the directions of page 459, the crust of arsenic cannot be mistaken for that of antimony. For by bringing the spirit-lamp flame under the crust when the stream of hydrogen has ceased to pass along the tube, if it be arsenic it rapidly volatilizes and condenses again on the neighbouring cool parts of the tube; the antimonial crust, on the contrary, when thus heated, fuses, runs into small globules, and assumes the appearance of mercury. If the tube be now detached from the vessel in which the hydrogen is generated, and the flame of the spirit-lamp cautiously applied to the metal, the arsenic volatilizes without fumes, and distinct octohedral crystals of arsenious acid are formed on the upper parts of the tube; with antimony, on the contrary, dense white fumes are produced and an amorphous white powder is deposited. The different characters of the two substances may be carried still further: if the tube be boiled in a small quantity of pure water, the arsenious acid is dissolved, and the first two tests may be successfully employed; the antimony, on the contrary, is insoluble.

Arsenic Acid.—This compound is made by dissolving arsenious acid in concentrated nitric, mixed with a little hydrochloric acid, distilling in glass till it acquires the consistence of syrup, and then exposing it in a platinum crucible for some time to a heat somewhat short of low redness to expel the nitric acid. The acid thus prepared has a sour metallic taste, reddens vegetable blue colours, and with alkalies forms neutral salts, which are termed *arseniates*. It is much more soluble in water than arsenious acid, dissolving in five or six times its weight of cold, and in a still smaller quantity of hot water. It forms irregular grains when its solution is evaporrated, but does not crystallize. If strongly heated, it fuses into a glass which is deliquescent. When urged by a very strong red heat, it is resolved into oxygen and arsenious acid. It is an active poison.

Arsenic acid is decomposed by hydrosulphuric acid gas, and yields a sulphuret of arsenic very like orpiment in colour, but containing a greater proportional quantity of sulphur. The soluble arseniates, when mixed with the nitrates of lead and silver, form insoluble arseniates, the former of which has a white, and the latter a brick-red colour. They dissolve readily in dilute nitric acid, and when heated with charcoal yield metallic arsenic.

Its eq. is 115·4; symb. $2As + 5O$, $\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{\text{As}}}$, or As_2O_5.

Protochloride of Arsenic.—It is prepared, according to Dumas, by introducing into a tubulated retort a mixture of arsenious acid with ten times its weight of concentrated sulphuric acid; and after raising its temperature to near 212°, fragments of sea-salt are thrown in by the tubular. If the salt is added in successive small portions, scarcely any hydrochloric acid gas is evolved, and the pure chloride may be collected in cooled vessels. Towards the end of the process a little water frequently passes over with the chloride; but this hydrated portion does not mix with the anhydrous chloride, but swims on its surface. The hydrate may be decomposed, and a pure chloride obtained, by distilling the mixture from a sufficient quantity of concentrated sulphuric acid. Dumas considers this compound a protochloride of arsenic, so that it is probably different from that obtained by means of corrosive sublimate. (Quarterly Journal of Science, N. S. i. 235.)

Its eq. is 73·12; symb. $As + Cl$, or $AsCl$.

Sesquichloride of Arsenic.—When arsenic in powder is thrown into a jar full of dry chlorine gas, it takes fire, and sesquichloride of arsenic is generated; and the same compound may be formed by distilling a mixture of six parts of corrosive sublimate with one of arsenic. It is a colourless volatile liquid, which fumes strongly on exposure to the air, hence called *fuming liquor of arsenic*, and is resolved by water into hydrochloric and arsenious acids. (Davy.)

Its eq. is 181·66; symb. $2As + 3Cl$, or As_2Cl_3.

Periodide of Arsenic is formed by bringing its elements into contact, and promoting union by gentle heat. They form a deep red compound, which is resolved into arsenic and hydriodic acids by the action of water. (Plisson in An. de Ch. et Ph. xxxix. 266.)

Its eq. is 706·9; symb. $2As + 5I$, or As_2I_5.

Sesquibromide of Arsenic.—The elements of this compound unite at the moment of contact, with vivid evolution of heat and light. Serullas prepared it by adding dry arsenic to bromine as long as light was emitted, the former being added in successive small quantities, to prevent the temperature from rising too high. The bromide is then distilled, and collected in a cool receiver. (An. de Ch. et Ph. xxxviii. 318.)

This compound is solid at or below 68°, liquefies between 68° and 77°, and boils at 428°. As a liquid it is transparent and slightly yellow, and yields long prisms by evaporation. By water it is resolved into arsenious and hydrobromic acids.

Its eq. is 313·6; symb. $2As + 3Br$, or As_2Br_3.

Protohyduret of Arsenic.—This compound, which is solid and of a brown colour, was discovered by Davy as well as Gay-Lussac and Thenard. The former prepared it by attaching a piece of arsenic to the negative wire during the decomposition of water by galvanism; and the French chemists, by the action of water on an alloy of potassium and arsenic.

Its eq. is 38·7; symb. $As + H$, or AsH.

Arseniuretted Hydrogen.—This gas, which was discovered by Scheele, has been studied by Proust, Trommsdorf, and others, but especially by Stromeyer. It is generally made by digesting an alloy of tin and arsenic in hydrochloric acid; but as thus prepared it is always mixed with free hydrogen. Soubeiran generated it by fusing arsenic with its own weight of granulated zinc, and decomposing the alloy with strong hydrochloric acid. The gas thus developed, is quite free from hydrogen, being absorbed without residue by a saturated solution of sulphate of oxide of copper. Its sp. gravity, according to Dumas, is 2·695. It is colourless, and has a fetid odour like that of garlic. It extinguishes bodies in combustion, but is itself kindled by them, and burns with a blue flame. It instantly destroys small animals that are immersed in it, and is poisonous to man in a high degree, having proved fatal to a German philosopher, the late M. Gehlen, and others. Water absorbs one-fifth of its volume, and acquires the odour of the gas. It is altogether destitute of the properties of an acid.

Arseniuretted hydrogen is decomposed by various agents. It suffers gradual decomposition when mixed with atmospheric air, water being formed, and metallic arsenic, together with a little oxide, deposited. With nitric acid, water is generated, and a deposite of metal takes place, which is subsequently oxidized. Chlorine decomposes it instantly with disengagement of heat and light, hydrochloric acid being generated, and the metal set free. With iodine it yields hydriodic acid gas and iodide of arsenic, and sulphur and phosphorus produce analogous changes. By its action on salts of the easily reducible metals, such as silver and gold, the metal is revived, and its oxygen uniting with the elements of the gas constitutes arsenious acid and water. With salts of copper the products are water and arseniuret of copper; and with several other metallic salts its action is similar.

Soubeiran observed that arseniuretted hydrogen in a glass tube is completely decomposed by the heat of a spirit-lamp, and that its hydrogen occupies one and a half as much space as when in combination. He has also confirmed the observation of Dumas, that when mixed with oxygen, and detonated by the electric spark, each volume of the gas, in forming water and arsenious acid, requires one and a half its volume of oxygen gas. The oxygen, therefore, is equally divided between the arsenic and hydrogen; and arseniuretted hydrogen consists of one eq. of arsenic and one and a half of hydrogen. By volume, it is composed of half a volume of the vapour of arsenic, and one and a half of hydrogen, condensed into one measure. (An. de Ch. et Ph. xliii. 407.)

Its eq. is 78·4; symb. $2As+3H$, or As_2H_3.

Sulphurets of Arsenic.—Sulphur unites with arsenic in at least three proportions, forming compounds, two of which occur in the mineral kingdom, and are well known by the names of *realgar* and *orpiment.* Realgar or the protosulphuret may be formed artificially by heating arsenious acid with about half its weight of sulphur, until the mixture is brought into a state of perfect fusion. The cooled mass is crystalline, transparent, and of a ruby-red colour; and may be sublimed in close vessels without change.

Its eq. is 53·8; symb. $As+S$, or AsS.

Orpiment, or *sesquisulphuret* of arsenic may be prepared by fusing together equal parts of arsenious acid and sulphur; but the best mode of obtaining it quite pure is by transmitting a current of hydrosulphuric acid gas through a solution of arsenious acid. Orpiment has a rich yellow colour, fuses readily when heated, and becomes crystalline on cooling, and in close vessels may be sublimed without change. It is dissolved with great facility by the pure alkalies, and yields colourless solutions.

Orpiment is employed as a pigment, and is the colouring principle of the paint called *King's yellow.* Braconnot has proposed it likewise for dyeing silk, woollen, or cotton stuffs of a yellow colour; the cloth being soaked in a solution of orpiment in ammonia, and then suspended in a warm apartment. The alkali evaporates, and leaves the orpiment permanently attached to the cloth. (An. de Ch. et Ph. xii.)

Its eq. is 123·7; symb. $2AS+3S$, or As_2S_3.

Persulphuret of arsenic is prepared by transmitting hydrosulphuric acid gas through a moderately strong solution of arsenic acid; or by saturating a solution of arseniate of potassa or soda with the same gas, and acidulating with hydrochloric or acetic acid. The oxygen of the acid unites with the hydrogen of the gas, and persulphuret of arsenic subsides. In colour it is very similar to orpiment, is dissolved by pure alkalies, fuses by heat, and may be sublimed in close vessels without decomposition.

Its eq. is 155·9; symb. $2As + 5S$, or As_2S_5.

The experiments of Orfila have proved that the sulphurets of arsenic are poisonous, though in a much less degree than arsenious acid. The precipitated sulphuret is more injurious than native orpiment. The only antidote of arsenious acid is hydrated peroxide of iron (Bunsen), the effects of which have been amply tested in Germany, and lately elucidated by Dr. D. Maclagan. (Edin. Med. and Surg. Journal, 1840.) It acts by forming an insoluble arsenite or arseniate; and must be used in the moist state, never having been dried; and also in large quantity. The late edition (1840) of the Edinburgh Pharmacopœia gives a process for preparing it for this object.

SECTION XVI.

CHROMIUM.—VANADIUM.

CHROMIUM.

Hist.—Discovered in the year 1797 by Vauquelin in a beautiful red mineral, the native dichromate of oxide of lead. (An. de Ch. xxv. and lxx.) It has since been detected in the mineral called *chromate of iron*, a compound of the oxides of chromium and iron, which occurs abundantly in several parts of the Continent, in America, and at Unst in Shetland. (Hibbert.) It derived its name from χρωμα, *colour*, owing to its remarkable tendency to form coloured compounds.

Prep.—By exposing the oxide of chromium mixed with charcoal to the most intense heat of a smith's forge; but owing to its strong affinity for oxygen, the reduction is extremely difficult. A better process, that of Vauquelin, is to mix the dry chloride into a paste with oil, place the mass in a crucible lined with charcoal, lute on a cover, and to expose it for an hour to a very strong heat. Liebig has obtained the metal in the form of a black powder, which acquires the metallic aspect from pressure, by heating the compound of terchloride of chromium and ammonia to redness, and transmitting over it dry ammoniacal gas: the chlorine unites with the hydrogen of the ammonia, hydrochloric acid and nitrogen gases are evolved, and pulverulent chromium remains. A still more convenient process is to decompose the sesquichloride by heat and ammoniacal gas, in which case the metal has a chocolate-brown colour. In this finely divided state it takes fire when heated in the open air. (An. de Ch. et Ph. xlviii. 297.)

Prop.—As obtained by Vauquelin's process it has a white colour with a shade of yellow, and a distinct metallic lustre. It is brittle, very infusible, and with difficulty attacked by acids, even by the nitro-hydrochloric. Its sp. gr. has been stated at 5·9; but Thomson found it a little above 5. When fused with nitre it is oxidized and converted into chromic acid. With a smaller quantity of oxygen it forms the green oxide.

From the experiments of Berzelius and Thomson the eq. of chromic acid may be estimated at 52; and as the salts of this acid are isomorphous with the sulphates and seleniates, it is inferred that chromic acid has the same atomic constitution as sulphuric and selenic acids, or consists of 1 eq. of chromium and 3 eq. of oxygen. Berzelius has moreover remarked that when the acid is converted into the green oxide of chromium, it parts with exactly half of its oxygen. Hence, 24 deducted from 52, leaves 28 as the eq. of chromium. Its symb. is Cr. The composition of its compounds described in this section is as follows:—

	Chromium.			Equiv.	Formulæ.
Sesquioxide	56	2 eq.+Oxygen	24	3 eq.= 80	2Cr+3O or Cr_2O_3.
Chromic Acid	28	1 eq.+ . .	24	3 eq.= 52	Cr+3O or CrO_3.
Sesquichloride	56	2 eq.+Chlorine	106·26	3 eq.=162·262	Cr+3Cl or Cr_2Cl_3.
Sesquifluoride	56	2 eq.+Fluorine	56·04	3 eq.=112·04	2Cr+3F or Cr_2F_3.
Perfluoride	Composition unknown.				
Sesquisulphuret	56	2 eq.+Sulphur	48·3	3 eq.=104·3	2Cr+3S or Cr_2S_3.
Protophosphuret	28	1 eq.+Phosphs.	15·7	1 eq.= 43·7	Cr+P or CrP.
Oxy-chloride	CrO_3 104	2 eq.+$CrCl_3$	106·26	1 eq.=210·26	$CrCl_3+2CrO_3$.

Sesquioxide of Chromium.—Prep.—This, the only known oxide of chromium, is prepared by dissolving chromate of potassa in water, and mixing it with a solution of nitrate of protoxide of mercury, when an orange-coloured precipitate, chromate of that oxide, subsides. On heating this salt to redness in an earthen crucible, the mercury is dissipated in vapour, and the chromic acid is resolved into oxygen and oxide of chromium. It may also be obtained in small tabular crystals by exposing the bichromate of potassa to a strong red heat; one eq. of chromic acid loses oxygen, while the other forms a neutral salt with the potassa. The latter is readily removed from the insoluble oxide by boiling water. Wöhler has succeeded in obtaining this oxide in fine crystals by conducting the vapour of the oxychloride of chromium (formerly terchloride of chromium) through a red-hot glass tube, when it is decomposed, oxide of chromium is deposited in fine crystals, and a mixture of oxygen and chlorine gases is evolved.

Prop.—As obtained by either of the first processes, it is a green powder; but the crystals of Wöhler are black and possess a strong metallic lustre, and are identical in form and very similar in appearance to specular iron ore: it is as hard as corundum, and has a sp. gr. of 5·21; its powder has the common green colour of oxide of chromium. (Pog. An. xxxiii. 341.)

It is insoluble in water, and after being strongly heated, resists the action of the most powerful acids. Deflagrated with nitre, or fused with chlorate of potassa, it is oxidized to its maximum, and is thus reconverted into chromic acid. Fused with borax or vitreous substances, it communicates to them a beautiful green colour, a property which affords an excellent test of its presence, and renders it exceedingly useful in the arts. The emerald owes its colour to the presence of this oxide.

Oxide of chromium is a salifiable base, and its salts, which have a green colour, may be easily prepared in the following manner. To a boiling solution of chromate of potassa in water, equal measures of strong hydrochloric acid and alcohol are added in successive small portions, until the red tint of the chromic acid disappears entirely, and the liquid acquires a pure green colour. On pouring an excess of pure ammonia into this solution, a pale green bulky hydrate subsides, which consists of 1 eq. of the oxide and 26 eq. of water. (Thomson.) The oxide, in this state, is readily dissolved by acids. On expelling the water by heat, the sudden approximation of the particles, which abruptly occurs at a certain temperature, causes such intense evolution of heat that the whole mass becomes vividly incandescent.

The anhydrous oxide is formed when bichromate of potassa is briskly boiled with sugar and a little hydrochloric acid. At first a brown matter falls, consisting of the acid and oxide of chromium; but subsequently the green oxide appears in the form of a finely divided powder. If the bichromate and sugar are employed without hydrochloric acid, the brown matter is the only solid product, and on boiling this compound with a little carbonate of potassa, a greenish-blue carbonate of chromium, of a very fine colour, is obtained. For this mode of preparation I am indebted to my late pupil, Mr. Thomas Thomson, of Clitheroe, near Manchester.

Its eq. is 80; symb. $2Cr + 3O$, $\underline{\dddot{Cr}}$, or Cr_2O_3.

Chromic Acid.—Prep.—This acid is best prepared by transmitting the gaseous fluoride of chromium into water contained in a vessel of silver or platinum, when by mutual decomposition of the gas and the water, hydrofluoric and chromic acids are generated: the former is then expelled by evaporating the solution to dryness, and the latter in a pure state remains. If the gas is conducted into a silver vessel which is only moistened with water, and the aperture of which is closed by a piece of moist paper, the chromic acid is obtained in the form of acicular crystals of a cinnabar red colour, which are so voluminous and abundant as to fill the interior of the vessel. Another method of preparing chromic acid has been suggested by Arnold Maus, which consists in decomposing a hot concentrated solution of bichromate of potassa by silicated hydrofluoric acid. The chromic acid, after being separated from the sparingly soluble fluoride of silicon and potassium, is evaporated to dryness in a platinum capsule, and then redissolved in the smallest possible quantity of water. By this means the last portions of the double salt are rendered insoluble, and the pure chromic acid may be separated by decantation. The acid must not be filtered in this concentrated state, as it then corrodes paper like sulphuric acid, and is converted into chromate of the green oxide of chromium. Asbestus, however, might be used for filtering this acid, in the same way as the permanganic acid. (Gregory.) When it is wished to prepare a large quantity of chromic acid by this process, porcelain vessels may be safely employed in the first part of the operation, provided care is taken to add a quantity of silicated hydrofluoric acid not quite sufficient for precipitating the whole of the potassa. (Edinburgh Journal of Science, viii. 175.)

It was formerly prepared by digesting chromate of baryta or oxide of lead in dilute sulphuric acid, the quantity of the latter being regulated with the view of decomposing the chromate without being in excess. A dark ruby-red solution is thus obtained, which by evaporation yields irregular crystals, and was supposed to contain pure chromic acid; but Gay-Lussac showed that the acid when thus procured is never pure, being intimately combined with sulphuric acid. On endeavouring to expel the latter by heat, the chromic acid itself yields oxygen, and is more or less completely converted into sulphate of the green oxide.

Prop.—Pure dry chromic acid is black while warm, and of a dark red colour when cold. It is very soluble in water, rendering it red or yellow according to the degree of dilution;—when the solution is concentrated by heat and allowed to cool, it deposits red crystals, which deliquesce readily in the air. In alcohol it is also soluble, but the action of heat or light causes its conversion into the green oxide. Its taste is sour, and with alkalies it acts as a strong acid. It is converted into the green oxide, with evolution of oxygen, by exposure to a strong heat. It yields a chloride when boiled with hydrochloric acid and alcohol, and the direct solar rays have a similar effect when hydrochloric acid is present: the mutual action sets chlorine free, and hence the solution acquires the property of dissolving gold. With sulphurous acid it forms a sulphate of the oxide; and it is more or less completely converted into the oxide by being boiled with sugar, starch, or various other organic principles. It destroys the colour of indigo, and of most vegetable and animal colouring matters; a property advantageously employed in calico-printing, and which manifestly depends on the facility with which it is deprived of oxygen.

Chromic acid is characterized by its colour, and by forming coloured salts with alkaline bases. The most important of these salts is chromate of oxide of lead, which is found native in small quantity, and is easily prepared by mixing chromate of potassa with a soluble salt of lead. It is of a rich yellow colour, and is employed in the arts of painting and dyeing to great extent. When heated to redness, it is also much used as the oxidizing agent in the ultimate analysis of organic substances. (Liebig.)

When sulphurous acid gas is transmitted into a solution of chromate or bichromate of potassa, a brown precipitate subsides, which was long regarded as a distinct oxide of chromium; but Thomson has proved that it is the green oxide combined with a little chromic acid. The acid may in a great measure be washed away by means of water, and by ammonia it is entirely removed; but the best mode of separating it, is to dissolve the brown matter with hydrochloric acid, and then precipitate the green oxide by ammonia. The brown compound may be formed by boiling a solution of bichromate of potassa with alcohol; and it is also rapidly generated, when bichromate of potassa is gently boiled with sugar and a very little hydrochloric acid.

Its eq. is 52; symb. $\mathrm{Cr} + 3\mathrm{O}$, $\overset{\cdots}{\mathrm{Cr}}$, or $\mathrm{CrO_3}$.

Sesquichloride of Chromium.—It is prepared by transmitting dry chlorine gas over a mixture of oxide of chromium and charcoal heated to redness in a tube of porcelain, when the sesquichloride gradually collects as a crystalline sublimate of a peach-purple colour, which in thin layers is transparent, but in thicker masses is opaque. Another method is to evaporate the green solution of this chloride gently to dryness at a temperature of 212°, when a green powder remains, consisting of 1 eq. of the sesquichloride and 3 eq. of water ($\mathrm{Cr_2Cl_3} + 3\dot{\mathrm{H}}$), these elements being exactly in the ratio to form oxide of chromium and hydrochloric acid. On raising the temperature above 212°, no water is lost until it reaches 400°: the powder then begins to swell up from the escape of water, the colour changes from green to the red of peach-blossoms, and pure sesquichloride remains. This part of the process should be conducted in a tube from which air is excluded by a current of dry carbonic acid gas. These phenomena are quoted by Liebig as favouring the notion that the green solution and powder are a hydrochlorate of an oxide, and not a chloride with water. Gregory has shown (Journ. de Pharm.) that the pink powder, first obtained by Kemp from the action of chloride of sulphur on oxychloride of chromium, is an isomeric modification of the sesquichloride above described. It is not crystalline, and quite insoluble in water; but by long exposure to air it passes slowly into the soluble state. Being formed at a high temperature, it probably differs from the soluble variety as ignited alumina, peroxide of iron, or sesquioxide of chromium, do from the same oxides previous to ignition. The existence of this modification has lately been confirmed by Rose. (Annalen der Pharm. 1840.)

The sesquichloride of chromium dissolves slowly, forming a deep green solution. The same may be prepared by directly dissolving the hydrated oxide in hydrochloric acid; or by digesting chromate of oxide of lead in strong hydrochloric acid, adding a little alcohol from time to time to promote the deoxidation of chromic acid, and then separating the resulting chloride of chromium from that of lead by strong alcohol, which together with any excess of hydrochloric acid is ultimately expelled by evaporating to dryness. Traces of lead which may have been dissolved are easily precipitated by hydrosulphuric acid.

Its eq. is 162·26; symb. $2\mathrm{Cr} + 3\mathrm{Cl}$, or $\mathrm{Cr_2Cl_3}$.

Sesquifluoride of Chromium is formed by dissolving the oxide in hydrofluoric acid, and evaporating the solution to dryness, when the sesquifluoride remains as a green crystalline residue, which is soluble in water. Its eq. is 112·04; symb. $2Cr + 3F$, or Cr_2F_3.

Perfluoride of Chromium.—Discovered by Unverdorben in 1825 (Ed. Journ. of Science, iv. 129). When a mixture of 3 parts of fluor-spar and 4 of chromate of oxide of lead is distilled with 5 parts of fuming or even common sulphuric acid in a leaden or silver retort, a red-coloured gas is disengaged, which acts rapidly upon glass, with deposition of chromic acid and formation of fluosilicic acid gas. It is decomposed by water, and the solution is found to contain a mixture of hydrofluoric and chromic acids. The watery vapour of the atmosphere effects its decomposition, so that when mixed with air, red fumes appear, owing to the separation of minute crystals of chromic acid.

The red colour of terfluoride of chromium naturally excites the suspicion that the gas itself may consist, not of fluoride of chromium, but of hydrofluoric and chromic acids; and its production by means of *hydrous* sulphuric acid is consistent with this idea. But since the gas may also be formed from fluor-spar, chromate of oxide of lead, and *anhydrous* sulphuric acid, it is clear that this view is inadmissible. It was formerly considered to be composed of 1 eq. of chromium and 3 eq. of fluorine, and was hence described as the terfluoride. H. Rose has shown, however, that its elements approximate more closely to the ratio of 1 to 5 rather than 1 to 3; but its true constitution is not yet satisfactorily determined. It is perhaps CrF_5.

Sulphuret of Chromium may be formed by transmitting the vapour of bisulphuret of carbon over oxide of chromium at a white heat; by heating in close vessels an intimate mixture of sulphur and the hydrated oxide; by fusing the oxide with a persulphuret of potassium, and dissolving the soluble parts in water; or by transmitting hydrosulphuric acid gas aided by heat over the sesquichloride of chromium. It cannot be prepared in the moist way. It is of a dark grey colour, and acquires metallic lustre by friction in a mortar. It is readily oxidized when heated in the open air, and is dissolved by nitric or nitro-hydrochloric acid.

Its eq. is 104·3; symb. $2Cr + 3S$, or Cr_2S_3.

Phosphuret of Chromium.—Rose prepared this compound by acting on the sesquichloride of chromium by phosphuretted hydrogen gas at a red heat. By mutual interchange of elements

1 eq. Sesquichloride	Cr_2Cl_3	yield	2 eq. Phosphuret	2CrP.
and 1 eq. Phosphur. Hyd.	P_2H_3		and 3 eq. Hydrochloric Acid.	3HCl.

This phosphuret is black, insoluble in hydrochloric acid, feebly attacked by nitric and nitro-hydrochloric acid, and burns before the blowpipe with a flame of phosphorus.

Its eq. is 43·7; symb. $Cr+P$, or CrP.

Another phosphuret of a grey colour may be formed by exposing the phosphate of oxide of chromium to a strong heat in a covered crucible lined with charcoal. Its composition is unknown.

Oxychloride of Chromium.—Hist.—Discovered by Unverdorben at the same time as the perfluoride of chromium: it was long considered and described as the terchloride, until Rose pointed out its real constitution. (Pog. An. xxvii. 565.)

Prep.—By the action of fuming sulphuric acid on a mixture of about equal weights of chromate of oxide of lead and chloride of sodium. Wöhler recommends the following process: 10 parts of chloride of sodium are fused in a common crucible with 16·9 parts of the neutral chromate of potassa, the fused salts are thrown upon a clean stone, and the mass when cold is broken into coarse fragments. These are to be introduced into a capacious tubulated retort, to which a receiver kept cold by moistened paper is adapted. Twelve parts of fuming sulphuric acid are then added to the fused salts, when an energetic action commences, and in a few minutes the oxychloride is formed and distilled over without the application of external heat. (Pog. An. xxxiii. 343.)

Prop.—It is a heavy red liquid, exceedingly volatile, yielding abundant red vapours when exposed to the air. By water it is instantly decomposed into hydrochloric and chromic acids. Its vapour is decomposed by a red heat into oxide of chromium, oxygen, and chlorine, as observed by Wöhler, who has thus confirmed the composition of the oxychloride as stated by Rose. The latter chemist found it was composed of 2 eq. of chromic acid and 1 eq. of a perchloride; and the former, that 2 eq. of the oxychloride produced 3 eq. of the oxide of chromium, 3 eq. of oxygen, and 6 eq. of chlorine. In symbols,

$$2\,(CrCl_3+2CrO_3) \quad \text{yield} \quad \left\{\begin{array}{l} 3Cr_2O_3. \\ 3O. \\ 6Cl. \end{array}\right.$$

Its eq. is 210·26; symb. $CrCl_3+2CrO_3$.

Millon considers it as chromic acid in which 1 eq. oxygen is replaced by chlorine, $Cr\left.\begin{array}{c} Cl \\ O_2 \end{array}\right\}$. The same ingenious chemist has extended this view to the bleaching compounds of chlorine. Thus bleaching powder, commonly viewed as $CaO, ClO + CaCl$, may be viewed as an oxychloride of calcium, $Ca\left.\begin{matrix}Cl\\O\end{matrix}\right\}$. For further details, I must refer to the foreign journals, as I have not been able to obtain the original memoir. (Editor.)

VANADIUM.

Hist.—Vanadium, so called from *Vanadis*, the name of a Scandinavian Deity, was discovered in the year 1830 by Sefström, of Fahlun, in iron prepared from the iron-ore of Taberg in Sweden. The state in which it occurs in the ore is unknown; but Sefström separated it from the iron by dissolving the latter in hydrochloric acid, when a black powder came into view containing a small quantity of vanadium, together with iron, copper, cobalt, silex, alumina, and lime. He afterwards found a more abundant source in the slag or cinder formed during the conversion of the cast-iron of Taberg into malleable iron. Soon after Sefström's discovery, the same metal was formed by Johnston, of Durham, in a mineral from Wanlockhead in Scotland, where it occurs as a vanadiate of oxide of lead. A similar mineral, found at Zimapan in Mexico, was examined in the year 1801 by Professor del Rio, who, in the belief of having discovered a new metal, gave it the name of *Erythronium*, apparently from the red colour of its acid; but as Collet Descotils, on being appealed to, declared the mineral to be chromate of lead, Del Rio abandoned his own opinion in deference to a higher authority. Thus have three persons noticed the existence of vanadium, without the knowledge of each other's labours; but the merit of being the first discoverer is fairly due to Sefström.*

Prep.—From the slag above-mentioned vanadic acid may be obtained by the following process, contrived by Sefström and improved by Berzelius. The slag in fine powder, mixed with its own weight of nitre and twice its weight of carbonate of potassa, is strongly ignited for the space of one hour. The soluble parts are then removed by boiling water, and the solution, after being filtered and neutralized with colourless nitric acid, is precipitated by chloride of barium or acetate of lead. The precipitate, which consists of vanadiate and phosphate of baryta or oxide of lead, zirconia, alumina, and silicic acid, is decomposed, while still moist, by digestion with strong sulphuric acid; to the deep-red solution, alcohol is then added, when by continued digestion ether is disengaged, and all the vanadic acid converted into the salifiable oxide, the solutions of which are blue; — a change effected in order the more completely to remove the vanadic acid from the insoluble matters. The blue liquid is then evaporated; and when it acquires a syrupy consistence, it is mixed in a platinum crucible with a little hydrofluoric acid, and sharply heated in an open fire. By this means the silicic acid, which can only be got rid of in this way, is converted into the gaseous fluoride of silicon, the sulphuric acid expelled, and the oxide reconverted into the acid of vanadium.

---

* Phil. Mag. and Annals, x. 321. An. de Ch. et Ph. xlvii. 337. Brewster's Journal, v. 318, N. S. Poggendorff's Annalen, xxii. 1.

The vanadic acid still contains phosphoric acid, alumina, and zirconia. For its further purification it is fused with nitre added in successive small portions, until, on cooling a small quantity, the red tint is found to have disappeared. In this process the acid of the nitre is displaced by the phosphoric and vanadic acids, the object being to cause those acids to unite with potassa without employing an excess of nitre. The vanadiate and phosphate of potassa are then taken up by as small a quantity of water as will suffice, and into the filtered liquid a piece of sal-ammoniac, larger than can be dissolved by it, is introduced: as it dissolves, vanadiate of ammonia, insoluble in a saturated solution of sal-ammoniac, subsides as a white powder, leaving the phosphoric acid in the liquid. The vanadiate of ammonia should be first washed with a solution of sal-ammoniac, and then with alcohol of sp. gr. 0·86.

By heating this salt in an open platinum crucible, vanadic acid is obtained; but the temperature ought to be kept below that of redness, and the mass be well stirred until it acquires a dark red colour. Heated in close vessels the vanadiate of ammonia is converted principally into the salifiable oxide; though some of the protoxide and acid are mixed with it. With the zirconia and alumina, left by the water after fusion with nitre, some vanadium remains: it may be extracted by fusion with sulphur and carbonate of potassa, when a double sulphuret of vanadium and potassium is generated, which is soluble in water. On adding sulphuric acid to the solution, sulphuret of vanadium is precipitated.

The preparation of vanadium from the native vanadiate of lead is much less complicated than the process above described. It suffices to dissolve the ore, as Johnston advises, in nitric acid, and to precipitate the lead by hydrosulphuric acid, which also throws down any arsenic that may be present. As vanadic acid is deoxidized by hydrosulphuric acid, a blue solution is formed; but by evaporating to dryness the acid is reproduced. The residue is then dissolved by a solution of ammonia, and the vanadiate of ammonia precipitated as before by a piece of sal-ammoniac. The vanadic acid is thus separated from arsenic, phosphoric, and hydrochloric acids, with which in the ore of Wanlockhead it is generally associated.

The attempts of Berzelius to reduce vanadic acid to the metallic state by the agency of hydrogen or charcoal at high temperatures proved unsuccessful, as the protoxide alone was obtained. He procured the metal, however, in the form of a heavy black powder, by placing fragments of fused vanadic acid and potassium of equal size in alternate layers in a porcelain crucible, the potassium being in the largest proportion: a cover was then luted on, and heat applied by means of a spirit-lamp. The reduction took place suddenly and with violence; and when the mass had cooled, the potassa and redundant potassium were separated by water. But Berzelius succeeded better by a process similar to that of H. Rose for procuring metallic titanium. The liquid chloride of vanadium is introduced into a glass bulb blown in a barometer tube, and through it is transmitted dry ammoniacal gas until a white saline mass is produced, during the formation of which the gas is rapidly absorbed, and heat disengaged. A spirit-lamp flame is then applied, which expels a quantity of hydrochlorate of ammonia, and metallic vanadium is left adhering to the interior of the bulb. The production of hydrochloric acid is obviously owing to chlorine leaving the vanadium and uniting with the hydrogen of part of the ammonia.

Prop.—The pulverulent vanadium, produced by means of potassium, has but little of the tenacity and appearance of a metal, though under strong pressure it assumes a lustre like that of graphite. Heated in the open air to commencing redness it takes fire, and is converted into the black protoxide. It conducts electricity, however, and is strongly electro-negative in relation to zinc. As procured by Rose's process the vanadium has a strong metallic lustre and a white colour considerably resembling silver, but still more like molybdenum. It is so extremely brittle that it cannot be removed from the glass bulb without falling into powder. It is not oxidized either by air or water; although by continued exposure to the air its lustre gradually grows weaker, and it acquires a reddish tint. It is not dissolved by boiling sulphuric, hydrochloric, or hydrofluoric acid; but by nitric and nitro-hydrochloric acid it is attacked, and the solution has a beautiful dark blue colour. It is not oxidized by being boiled with caustic potash, nor by carbonated alkalies at a red heat.

The eq. of vanadium, according to the analysis of its oxides by Berzelius, is 68·5; its symb. is V; and its compounds described in this section are thus constituted:—

	Vanadium.			Equiv.	Formulæ.
Protoxide	68·5	1 eq.+Oxygen	8	1 eq.= 76·5	$V+O$ or VO.
Binoxide	68·5	1 eq.+ do.	16	2 eq.= 84·5	$V+2O$ or VO_2.
Vanadic Acid	68·5	1 eq.+ do.	24	3 eq.= 92·5	$V+3O$ or VO_3.
Bichloride	68·5	1 eq.+Chlorine	70·84	2 eq.=139·34	$V+2Cl$ or VCl_2.
Terchloride	68·5	1 eq.+ do.	106·26	3 eq.=174·76	$V+3Cl$ or VCl_3.
Bibromide	68·5	1 eq.+Bromine	156·8	2 eq.=225·3	$V+2Br$ or VBr_2.
Bisulphuret	68·5	1 eq.+Sulphur	32·2	2 eq.=100·7	$V+2S$ or VS_2.
Tersulphuret	68·5	1 eq.+ do.	48·3	3 eq.=116·8	$V+3S$ or VS_3.

Protoxide.—This compound is readily formed from vanadic acid by the combined agency of heat and charcoal or hydrogen gas. By means of the latter Berzelius found that the reduction is effected as perfectly at a temperature short of ignition, as at the strongest heat of a wind furnace. When prepared from fused vanadic acid, the protoxide retains the crystalline structure of the acid, and has a black colour and a semi-metallic lustre; but it is easily broken down into a fine black powder. When rendered coherent by compression it possesses a property very unusual in oxides, that of conducting electricity, and in relation to zinc of being as strongly electro-negative as silver or copper.

It is very infusible. When heated in open vessels it takes fire and burns like tinder, being converted into the binoxide. On exposure to air and moisture it is slowly oxidized, a process which is best seen by putting it into water, when the liquid gradually acquires a green tint. In both cases the oxygen is derived from the atmosphere. A similar change occurs in acid and alkaline solutions, which, with the exception of nitric acid, do not dissolve it even at a boiling temperature. Heated in nitric acid oxidation ensues with escape of nitric oxide gas, and a blue nitrate of the binoxide of vanadium is generated. The character of an alkaline base seems wholly wanting in the protoxide, and hence Berzelius considers it as a *sub-oxide.* Its eq. is 76·5; symb. $V+O$, $\dot{V}$, or VO.

Binoxide.—*Prep.*—Best prepared, in the dry way, by heating to full redness an intimate mixture of 10 parts of the protoxide with 12 of vanadic acid in a vessel filled with carbonic acid, or from which combustible matter on the one hand, and oxygen gas on the other, are carefully excluded. From the salts of the binoxide, and especially the sulphate, it is precipitated as a greyish-white hydrate by means of a very slight excess of carbonate of soda. The residual solution is colourless when the process has been properly conducted: it remains blue, from undecomposed salt, if an insufficient quantity of alkali is used; it is brown when the alkaline carbonate is too freely employed, because some of the binoxide is then dissolved by the free alkali; and if the solution contained vanadic acid, its colour after precipitation is green. The presence of the latter is avoided by transmitting hydrosulphuric acid gas into the solution, whereby vanadic acid is effectually converted into the binoxide, but the redundant gas should be expelled by gentle heat before the oxide is precipitated. As the hydrate, while moist, readily absorbs oxygen, and hence acquires a tint of brown, it must be washed and dried without exposure to the air. When thus prepared it retains its grey tint. By exposure to heat in a vessel from which the air is excluded, it gives out water, and acquires all the characters of the oxide prepared in the dry way.

Prop.—A black pulverulent substance, very infusible, insoluble in water, and free from any acid or alkaline reaction. When heated in the open air it is converted into vanadic acid, and when moist it gradually suffers the same change at ordinary temperatures. It is dissolved by acids more readily as a hydrate than after being heated to redness, and forms salts, most of which have a blue colour, and are more or less soluble in water. They may all be conveniently formed by the direct action of acids on the hydrated oxide. The nitrate may be made by acting on vanadium, or either of its oxides, by nitric acid; the salt, when diluted with water, may be boiled without change; but when evaporated, even spontaneously, the blue colour passes through green into red, owing to the production of vanadic acid. The sulphate is easily prepared by dissolving vanadic acid in warm sulphuric acid diluted with an equal weight of water, decomposing the vanadic acid by hydrosulphuric acid, concentrating the solution in order that the salt may be deposited, and washing away adhering sulphuric acid by means of alcohol. The deoxidation of vanadic acid in the preceding process may also be effected by adding pure oxalic acid as long as carbonic acid gas is evolved.

The salts of the binoxide of vanadium are distinguished by their blue colour, by yielding with the alkalies or their carbonates in very slight excess the hydrated binoxide, which becomes red by oxidation, and by forming with solution of gall-nuts a black compound, a tannate of the binoxide, very similar to ink.

The binoxide is disposed to act the part of an acid by uniting with alkaline bases, with which it forms definite, and in some cases crystalline, compounds. On digesting the hydrated binoxide in pure potassa or ammonia, combination is readily effected, and a dark brown solution is formed. These compounds, though soluble in water, are very sparingly so in strong and cold alkaline solutions, and may be precipitated by them. Most of the other salts formed by the binoxide and salifiable bases are insoluble in water, and may be formed from the preceding by way of double decomposition.

Its eq. is 84·5 ; symb. $V + 2O$, $\ddot{V}$, or VO_2.

Vanadic Acid.—When vanadiate of ammonia, prepared as already mentioned, is heated in close vessels, the acid is decomposed by the hydrogen of the ammonia, and binoxide of vanadium is formed, mixed with a little protoxide and undecomposed acid. If the salt is heated in an open vessel, and well stirred, the whole mass acquires a dark red colour, and pure vanadic acid is obtained: but a red heat should be avoided, since fusion would thereby be occasioned, and free exposure of every part to the atmosphere prevented. Its colour in the state of fine powder is a light rust-yellow; but the fused acid is red with a shade of orange, and has a strong lustre. By light transmitted through thin layers it appears yellow. In the fire it is fixed, and is not decomposed by a very strong heat, provided combustible matters are excluded. It fuses at a heat lower than that of redness, and crystallizes readily as it cools. In the act of becoming solid it contracts considerably in volume, and emits so much heat of fluidity that the acid, after ceasing to be luminous, is again rendered incandescent, and remains so until the congelation is complete.

It is tasteless, insoluble in alcohol, and very slightly soluble in water, which takes up rather less than 1-100th of its weight, acquiring a yellow colour and an acid reaction. Heated with combustible matter it is deoxidized, being converted into the protoxide or binoxide or mixtures of these oxides. In solutions it is deprived of oxygen by all deoxidizing agents, such as alcohol, sugar, and most organic substances, including the oxalic and several vegetable acids, by hydrosulphuric acid and most of the other hydracids, not excepting the hydrochloric, by sulphurous and phosphorous acids, and even by nitrous acid. Like molybdic and tungstic acids it is disposed to act as a base to such of the stronger acids as do not decompose it, and to form with them definite compounds, which are soluble in water. It unites on this principle with sulphuric and phosphoric acid; and Berzelius has remarked a compound of the phosphoric, silicic, and vanadic acids, a sort of double salt, in which the latter acid is a base to the two former, and which crystallizes in scales; it is formed in Sefström's process for preparing vanadic acid, and its solubility opposes a great obstacle to the separation of vanadic from silicic acid.

Vanadic acid unites with salifiable bases often in two or more proportions, forming soluble salts with the alkalies, and in general sparingly soluble salts with the other metallic oxides. Those with excess of acid are commonly of a red or orange-red colour. Most of the neutral salts are yellow; but it is singular that the neutral vanadiates of the alkalies, the alkaline earths, and the oxides of lead, zinc, and cadmium may be yellow at one time and colourless at another without suffering any appreciable change in composition. Thus, on neutralizing vanadic acid with ammonia a yellow salt is obtained, the solution of which gradually becomes colourless if kept for some hours, and suffers the same change rapidly when heated. The solution, as it is coloured or colourless, gives a yellow or white residue by evaporation, and a yellow or white precipitate with a salt of baryta or oxide of lead. These changes appear to be of the same kind as those already noticed in the description of phosphoric acid.

Vanadic acid unites in different proportions with binoxide of vanadium, and forms compounds which are soluble in pure water, but sparingly so in saline solutions, and which are purple, green, yellow, or orange, according as the acid is in a smaller or larger proportion. They are best formed by exposing the hydrated binoxide to the atmosphere, when these different colours successively appear, as a gradually increasing quantity of the acid is generated.

Vanadic acid is distinguished from all other acids except the chromic by its colour, and from this acid by the action of deoxidizing substances, which give a blue solution with the former and a green with the latter. When heated with borax in the reducing flame of the blowpipe, both of the acids yield a green glass; but in the oxidizing flame the bead becomes yellow if vanadium is present, while the green colour produced by chromium is permanent.

Its eq. is 92·5; symb. $V + 3O$, $\dddot{V}$, or VO_3.

Chlorides.—The bichloride is prepared by digesting a mixture of the vanadic and hydrochloric acids, deoxidizing any undecomposed vanadic acid by hydrosulphuric acid, and evaporating the solution to dryness. A brown residue is obtained, which yields a blue solution with water, part being left as an insoluble sub-salt. It may also be generated by acting directly on the ignited binoxide with strong hydrochloric acid. As thus obtained its solution is brown instead of blue, though in composition it seems identical with the preceding. Its eq. is 139·34; symb. $V + 2Cl$, or VCl_2.

The *terchloride* may be formed by transmitting a current of dry chlorine gas over a mixture of protoxide of vanadium and charcoal heated to a low redness, when the terchloride passes over in vapour, and condenses in the form of a yellow liquid, from which free chlorine may be removed by a current of dry air. It is converted by water into hydrochloric and vanadic acid, and atmospheric humidity produces the same change, which is indicated by the escape of red fumes. Its eq. is 174·76; symb. $V + 3Cl$, or VCl_3.

A *bibromide* of vanadium may be formed in the same manner as the bichloride, substituting the hydrobromic for hydrochloric acid. Similar compounds may be procured with iodine, fluorine, and cyanogen by dissolving binoxide of vanadium in hydriodic, hydrofluoric, and hydrocyanic acid.

Sulphurets.—When the binoxide of vanadium is heated to redness in a current of hydrosulphuric acid gas, it is converted into protoxide, and both water and sulphur are obtained: on continuing the process, the protoxide is decomposed, hydrogen gas and water pass over, and bisulphuret of vanadium is generated. This compound may also be procured by mixing sulphate of ammonia with a salt of the binoxide of vanadium until the precipitate at first formed is redissolved, and then decomposing the deep purple-coloured solution by sulphuric or hydrochloric acid. The bisulphuret of a brown colour subsides, which becomes black when it is dried. It is unchanged at common temperatures by exposure to the air, but takes fire when heated. In the hydrated state it is dissolved by alkalies and alkaline sulphurets; but it is insoluble in acids, with the exception of the nitric and nitro-hydrochloric, by which it is converted into sulphate of the binoxide.

Its eq. is 100·7; symb. $V + 2S$, or VS_2.

When hydrosulphuric acid gas is transmitted through an aqueous solution of vanadic acid, a greyish-brown precipitate is formed, consisting of hydrated binoxide of vanadium mixed mechanically with sulphur. But if a solution of vanadic acid in hydrosulphate of ammonia is acidulated by hydrochloric or sulphuric acid, the hydrated *tersulphuret* of vanadium subsides. Its colour is of a much lighter brown than the bisulphuret, becomes almost black in drying, and is resolved by a red heat in close vessels into the bisulphuret with loss of water and sulphur. It is soluble in alkalies and alkaline sulphurets, and is oxidized by nitric acid.

Its eq. is 116·8: symb. $V + 3S$, or VS_3.

The phosphuret of vanadium, of a leaden-grey colour, may be formed by exposing to a white heat phosphate of the binoxide of vanadium mixed with a small quantity of sugar.

SECTION XVII.

MOLYBDENUM.—TUNGSTEN.—COLUMBIUM.

MOLYBDENUM.

Hist. and Prep.—The principal ore of molybdenum is the sulphuret, which was long mistaken for graphite, and was first distinguished from it in 1778 by Scheele; but the metal was obtained in a separate state by Hjelm. When this ore, in fine powder, is digested in nitro-hydrochloric acid until it is completely decomposed, and the residue is briskly heated in order to expel sulphuric acid, molybdic acid remains in the form of a white heavy powder. From this acid metallic molybdenum may be obtained by exposing it with charcoal to the strongest heat of a smith's forge; or by conducting over it a current of hydrogen gas while strongly heated in a tube of porcelain. (Berzelius.) Molybdenum likewise occurs in nature in the form of molybdate of oxide of lead.

Prop.—It is a brittle metal, of a white colour, and so very infusible, that hitherto it has only been obtained in a state of semifusion. In this form it has a sp. gr. varying between 8·615 and 8·636. When heated in open vessels it absorbs oxygen, and is converted into *molybdic acid;* and the same compound is generated by the action of chlorine or nitro-hydrochloric acid. It has three degrees of oxidation, forming two oxides and one acid, from the composition of which Berzelius estimates the eq. of moybdenum at 47·7. Its symb. is Mo. The composition of its compounds described in this section is as follows:—

	Molybdenum.			Equiv.	Formulæ.
Protoxide	47·7	1 eq.+Oxygen	8	1 eq.= 55·7	$Mo+O$ or MoO.
Binoxide	47·7	1 eq.+do.	16	2 eq.= 63·7	$Mo+2O$ or MoO_2.
Molybdic Acid	47·7	1 eq.+do.	24	3 eq.= 71·7	$Mo+3O$ or MoO_3.
Protochloride	47·7	1 eq.+Chlorine	35·42	1 eq.= 83·12	$Mo+Cl$ or $MoCl$.
Bichloride	47·7	1 eq.+do.	70·84	2 eq.=118·54	$Mo+2Cl$ or $MoCl_2$.
Bisulphuret	47·7	1 eq.+Sulphur	32·2	2 eq.= 79·9	$Mo+2S$ or MoS_2.
Tersulphuret	47·7	1 eq.+do.	48·3	3 eq.= 96·0	$Mo+3S$ or MoS_3.
Persulphuret	47·7	1 eq.+do.	64·4	4 eq.=112·1	$Mo+4S$ or MoS_4.
Oxychloride	MoO_3 143·4	2 eq.+$MoCl_3$	153·96	1 eq.=297·36	$2MoO+MoCl_3$.

Protoxide of Molybdenum.—On dissolving molybdate of potassa or soda in a small quantity of water, adding hydrochloric acid until the molybdic acid at first thrown down is redissolved, and digesting with a piece of pure metallic zinc, the latter deoxidizes the molybdic acid, the liquid changes to blue, red, and black, and then contains chloride of zinc and protochloride of molybdenum. From the black solution pure potassa throws down the protoxide of molybdenum as a black hydrate, an excess of the alkali being used in order to hold the zinc in solution. The hydrate is washed with the least possible exposure to the air, and dried in vacuo by sulphuric acid. When heated to low redness in the open air it takes fire and is converted into the binoxide; but if not exposed to the air it becomes incandescent at the moment of losing its water, like hydrated oxide of chromium. The anhydrous oxide is black and insoluble in acids; but in the state of hydrate, acids dissolve it. The recently precipitated hydrate is soluble in the cold by carbonate of ammonia, but in none of the other alkalies.

Its eq. is 55·7; symb. $Mo + O$, $\dot{Mo}$, or MoO.

Binoxide of Molybdenum.—Prep.—Obtained as a deep brown anhydrous powder by mixing molybdate of soda with half its weight of sal-ammoniac in fine powder, projecting the mixture into a red-hot crucible, which is to be instantly covered, and the heat continued until vapours of sal-ammoniac cease to appear. In this process chloride of sodium is generated, and molybdic acid is reduced by the ammonia to the state of binoxide: by adding water to the mass when cold chloride of sodium is dissolved, and the dark brown, nearly black, binoxide left. The hydrate, of a rust-brown colour, may be formed by digesting molybdenum in powder with molybdic acid dissolved in hydrochloric acid, until the liquid acquires a deep red colour, and then adding ammonia; or by adding ammonia to a solution of the bichloride; or digesting with metallic copper a solution of molybdic in hydrochloric acid until a deep red solution is formed, and employing an excess of ammonia in order to keep oxide of copper in solution.

Prop.—The anhydrous binoxide is insoluble in acids and is changed into molybdic acid by strong nitric acid. The hydrate is very like hydrated peroxide of iron, reddens litmus paper when placed on it, is dissolved by acids with which it forms red salts, is insoluble in the alkalies, but dissolves in alkaline carbonates. It is soluble, though sparingly, in pure water, so that it should be washed after precipitation by a solution of sal-ammoniac, which salt is afterwards removed by alcohol. On exposure to the air, the hydrate absorbs oxygen and becomes blue at its surface: this blue compound is more soluble in water than the hydrate, and was supposed by Bucholz to be a distinct acid, which he termed *molybdous acid;* but Berzelius has shown that it is a bimolybdate of the binoxide. (Berzelius.)

Its eq. is 63·7; symb. $Mo + 2O$, $\overset{\cdot\cdot}{Mo}$, or MoO_2.

Molybdic Acid.—Prep.—When sulphuret of molybdenum is roasted in an open crucible kept at a low red heat, and constantly stirred until sulphurous acid ceases to escape, a dirty yellow powder is left, which contains impure molybdic acid. The acid is taken up by ammonia and the filtered solution evaporated to dryness; it is again taken up by a little dilute ammonia and filtered; it is then purified by crystallization. On heating gently in an open platinum crucible, taking care to prevent fusion, the ammonia is expelled, and pure acid remains. It is also obtained by oxidizing the binoxide with nitric acid.

Prop.—As thus formed, it is a white powder, of sp. gr. 3·49, fusible by a red heat into a yellow liquid, which bears a strong red heat in closed vessels without subliming, but in an open crucible rises with the current of air, and collects on cold surfaces in colourless crystalline scales. It requires 570 times its weight of water for solution, which nevertheless has an acid reaction. It is soluble in the alkalies, forming colourless molybdates, from which molybdic acid is precipitated by the stronger acids, though an excess of the acids dissolves it; but after exposure to a red heat it is insoluble in acids.

Chlorides.—Berzelius has described three chlorides of molybdenum which he considered analogous in composition to the oxides; but his terchloride has recently been shown by Rose to be an oxychloride which has the same constitution as the oxychloride of chromium. (Pog. An. xl. 395.)

The protochloride is formed by dissolving the hydrated protoxide in hydrochloric acid, when it forms a deep nearly black coloured solution, which leaves a black viscid mass by evaporation.

Its eq. is 83·12; symb. $Mo + Cl$, or $MoCl$.

The *bichloride* is obtained as above mentioned, and yields a red solution. It is obtained in the anhydrous state by gently heating molybdenum in powder in dry chlorine gas, atmospheric air being excluded. The metal takes fire at its surface, but it is soon extinguished, after which the chlorine is replaced by a red vapour of such intensity that it is completely opaque in a vessel $\frac{3}{4}$ inch in diameter: this vapour condenses in the cooler parts of the apparatus in brilliant black crystals just like those of iodine, which are very fusible, and sublime at a gentle heat. Exposed to dry oxygen gas it is transformed gradually into oxychloride of molybdenum and molybdic acid. With water the bichloride acts violently from the intense heat evolved, and the whole is dissolved.

Its eq. is 118·54; symb. $Mo + 2Cl$, or $MoCl_2$.

Sulphurets.—Molybdenum combines with sulphur in three proportions. The lowest grade is the *bisulphuret*, which is the most common ore of molybdenum, and is usually associated with ores of tin, has a lead-grey colour and metallic lustre resembling graphite, for which it was formerly mistaken. Its density varies from 4·138 to 4·569. It bears a strong heat in close vessels without change or fusion; but it is oxidized by nitric acid or by the joint action of heat and air. Its eq. is 79·9; symb. $Mo + 2S$, or MoS_2.

The *tersulphuret* is obtained by saturating molybdate of potassa, soda, or ammonia with hydrosulphuric acid gas, and adding hydrochloric acid, when the tersulphuret falls of a deep brown colour, which becomes black on drying. It is partially oxidized when dried in the air. By heat in close vessels it is changed into the bisulphuret with loss of sulphur.

Its eq. is 96; symb. $Mo + 3S$, or MoS_3.

The persulphuret is made by boiling the sulphur-salt formed of tersulphuret of molybdenum and sulphuret of potassium for a long time with the bisulphuret of molybdenum, when a precipitate collects which is to be well washed with cold water. It is a sulphur-salt composed of persulphuret of molybdenum and sulphuret of potassium, which forms with boiling water a deep red solution, from which on the addition of hydrochloric acid the persulphuret subsides.

Its eq. is 112·1; symb. $MO + 4S$, or MoS_3.

Oxychloride of Molybdenum.—Formerly described as a terchloride. It is obtained by heating the binoxide in a current of dry chlorine. It is white with a shade of yellow, sublimes at a heat short of redness, and condenses into crystalline scales. It dissolves in water, but the solution is slightly milky from the separation of molybdic acid. From its composition, which has been recently determined by Rose, it would appear that

3 eq. of Binoxide and	3 eq. of Chlorine	yield	1 eq. of Oxychloride
$3\ MoO_2$	$3Cl$		$MoCl_3+2MoO_3$.

Its eq. is 297·36; symb. $MoCl_3 + 2MoO_3$.

TUNGSTEN.

It derives its name from the Swedish words *Tung Sten, heavy stone*, from the density of its ores; and it is called Wolfram from the mineral of that name, which is a tungstate of the oxides of iron and manganese. This metal may be procured in the metallic state by exposing tungstic acid to the action of charcoal or dry hydrogen gas at a red heat; but though the reduction is easily effected, an exceedingly intense temperature is required for fusing the metal. Tungsten has a greyish-white colour, and considerable lustre. It is brittle, nearly as hard as steel, and less fusible than manganese. Its sp. gr. is near 17·4. When heated to redness in the open air it takes fire, and is converted into tungstic acid; and it undergoes the same change by the action of nitric acid. Digested with a concentrated solution of pure potash, it is dissolved with disengagement of hydrogen gas, and tungstate of potash is generated.

Chemists are acquainted with two compounds of this metal and oxygen; namely, the *dark brown oxide*, and the *yellow acid of tungsten;* and according to the analyses of Berzelius, (An. de Ch. et Ph. xvii.) the oxygen of the former is to that of the latter in the ratio of two to three. From the composition of the latter, and assuming that it contains three atoms of oxygen, the eq. of tungsten is 99·7. Its symb. is W. Its compounds described in this section are thus constituted:—

	Tungsten.			Equiv.	Formulæ.
Binoxide	99·7	1 eq.+Oxygen	16	2 eq. = 115·7	$W+2O$ or WO_2.
Blue Oxide	199·4	2 eq.+ditto	24	3 eq. = 223·4	$2W+3O$ or W_2O_3.
Tungstic Acid	99·7	1 eq.+ditto	24	3 eq. = 123·7	$W+3O$ or WO_3.
Bichloride	99·7	1 eq.+Chlorine	70·84	2 eq. = 170·54	$W+2Cl$ or WCl_2.
Bisulphuret	99·7	1 eq.+Sulphur	32·2	2 eq. = 131·9	$W+2S$ or WS_3.
Persulphuret	99·7	1 eq.+ditto	48·3	3 eq. = 148·0	$W+3S$ or WS_2.
Oxychloride	WO_3 257·4	2 eq.+WCl_3	205·96	1 eq. = 463·36	WCl_3+2WO_3.

Binoxide.—*Prep.*—By the action of hydrogen gas on tungstic acid at a low red heat; but the best mode of procuring it, both pure and in quantity, is that recommended by Wöhler. (Quarterly Journal of Science, xx. 177.) This process consists in mixing Wolfram in fine powder with twice its weight of carbonate of potassa, and fusing the mixture in a platinum crucible. The resulting tungstate of potassa is dissolved in hot water, mixed with about half its weight of hydrochlorate of ammonia in solution, evaporated to dryness, and exposed in a hessian crucible to a red heat. The mass is well washed with boiling water, and the insoluble matter digested in dilute potassa to remove any tungstic acid. The residue is oxide of tungsten. It appears that in this process the tungstate of potassa and hydrochlorate of ammonia mutually decompose each other, so that the dry mass consists of chloride of potassium and tungstate of ammonia. The elements of the latter react on each other at a red heat, giving rise to water, nitrogen gas, and oxide of tungsten; and this compound is protected from oxidation by the fused chloride of potassium with which it is enveloped. This oxide is also formed by putting tungstic acid in contact with zinc in dilute hydrochloric acid. The tungstic acid first becomes blue, and then assumes a copper colour; but the oxide in this state can with difficulty be preserved, as by exposure to the air, and even under the surface of water, it absorbs oxygen, and is reconverted into tungstic acid.

Prop.—When prepared by means of hydrogen gas, it has a brown colour, and when polished acquires the colour of copper; but when procured by Wöhler's process, it is nearly black. It does not unite, so far as is known, with acids; and when heated to near redness, it takes fire and yields tungstic acid.

Its eq. is 115·7; symb. $W + 2O$, $\ddot{W}$, or WO_2.

Tungstic Acid.—*Prep.*—Conveniently by digesting native tungstate of lime, very finely levigated, in nitric acid; by which means nitrate of lime is formed, and tungstic acid separated in the form of a yellow powder. Long digestion is required before all the lime is removed; but the process is facilitated by acting upon the mineral alternately by nitric acid and ammonia. The tungstic acid is dissolved readily by that alkali, and may be obtained in a separate state by heating the tungstate of ammonia to redness. Tungstic acid may also be prepared by the action of hydrochloric acid on Wolfram. It is also obtained by heating the brown oxide to redness in open vessels.

Prop.—Tungstic acid is of a yellow colour, is insoluble in water, and has no action on litmus paper. With alkaline bases it forms salts called *tungstates*, which are decomposed by the stronger acids, the tungstic acid in general falling combined with the acid by which it is precipitated. When strongly heated in open vessels it acquires a green colour, and becoms blue when exposed to the action of hydrogen gas at a temperature of 500° or 600° F. The blue compound, according to Berzelius, is a tungstate of the oxide of tungsten; and the green colour is probably produced by an admixture of this compound with the yellow acid.

Its eq. is 123·7; symb. $W + 3O$, $\dddot{W}$, or WO_3.

Malaguti finds that the blue compound, formed in the manner stated above, is never constant in its composition; but he obtained a definite compound by heating tungstic acid by the flame of a spirit-lamp in a current of dry hydrogen. According to his analysis it contains 17·72 per cent. of oxygen; and he considers it a distinct acid, the constitution of which is represented by the symb. $2W + 5O$, or W_2O_5. (An. de Ch. et Ph. lx. 271.)

Chlorides of Tungsten.—Tungsten and chlorine unite in two proportions. When metallic tungsten is heated in chlorine gas, it takes fire, and yields the bichloride. The compound appears in the form of delicate needles, of a deep red colour resembling wool, but more frequently as a deep-red fused mass which has the brilliant fracture of cinnabar. When heated, it fuses, boils, and yields a red vapour. By water it is changed into hydrochloric acid and oxide of tungsten. It is entirely dissolved by solution of pure potassa, with disengagement of hydrogen gas, yielding tungstate of potassa and chloride of potassium. A similar change is produced by ammonia, except that some oxide of tungsten is left undissolved.

Its eq. is 170·54; symb. $W + 2Cl$, or WCl_2.

Another chloride has been described by Wöhler. It is formed at the same time as the first; by the action of water it is converted into hydrochloric and tungstic acids. It is the most beautiful of all these compounds, existing in long transparent crystals of a fine red colour. It is very fusible and volatile, and its vapour is red like that of nitrous acid. The difference between this compound and the chloride first described is not yet satisfactorily determined; for although the analysis of Malaguti in his paper above referred to would indicate its constitution to be similar to that of his blue oxide, and therefore W_2Cl_5, still the errors into which he fell in reference to the terchloride throw suspicion on this result. The production of tungstic acid by its decomposition with water strengthens this suspicion.

Sulphurets of Tungsten.—The protosulphuret is obtained as a black powder by transmitting hydrosulphuric acid gas, or the vapour of sulphur, over tungstic acid heated to whiteness in a tube of porcelain. The persulphuret is prepared by dissolving tungstic acid in a solution of sulphuret of potassium or hydrosulphate of ammonia, and adding an excess of hydrosulphuric acid. It falls as a brown precipitate, which becomes black in drying. It is soluble to a certain extent in water which is free from saline matter.

Oxychloride of Tungsten.—Formerly described as the terchloride. It was discovered by Wöhler, and prepared by heating the binoxide of tungsten in a stream of dry chlorine gas. The action is attended with the appearance of combustion, dense fumes arise, and a thick sublimate is obtained in the form of scales, like native boracic acid. It is volatile at a low temperature without previous fusion. According to Rose, who has determined its composition, (Pog. An. xl. 395,) it is resolved when suddenly heated into tungstic acid, the birchloride of tungsten, and chlorine.

Its eq. is 463·36 ; symb. $WCl_3 + 2WO_3$; or, as in the case of the corresponding compound of chromium, $W\left.\begin{matrix}Cl\\O_2\end{matrix}\right\}$.

COLUMBIUM.

Hist.—This metal was discovered in 1801 by Hatchett, who detected it in a black mineral belonging to the British Museum, supposed to have come from Massachusets in North America; and from this circumstance applied to it the name of *columbium.* About two years after, M. Ekeberg, a Swedish chemist, extracted the same substance from *tantalite* and *yttro-tantalite;* and, on the supposition of its being different from columbium, described it under the name of *tantalum.* The identity of these metals, however, was established in the year 1809 by Wollaston.

Prep.—Columbic acid is with difficulty reduced to the metallic state by the action of heat and charcoal; but Berzelius succeeded in obtaining this metal by the same process which he employed in the preparation of zirconium and silicon, namely, by heating potassium with the double fluoride of potassium and columbium. On washing the reduced mass with hot water, in order to remove the fluoride of potassium, columbium is left in the form of a black powder.

Prop.—As a powder it does not conduct electricity; but in a denser state it is a perfect conductor. By pressure it acquires metallic lustre, and has an iron-grey colour. It is not fusible at the temperature at which glass is fused. When heated in the open air it takes fire considerably below the temperature of ignition, and glows with a vivid light, yielding columbic acid. It is scarcely at all acted on by the sulphuric, hydrochloric, or nitro-hydrochloric acid; whereas it is dissolved with heat and disengagement of hydrogen gas by hydrofluoric acid, and still more easily by a mixture of nitric and hydrofluoric acids. It is also converted into columbic acid by fusion with hydrate of potassa, the hydrogen gas of the water being evolved.

From the experiments of Berzelius on the composition of the oxide and acid of columbium, its eq. may be estimated at 185. Its symb. is Ta. The compounds described in this section are thus constituted:—

	Columbium.				Equiv.	Formulæ.
Binoxide .	185	1 eq.+Oxygen	16	2 eq.=	201	$Ta+2O$ or TaO_2.
Columbic Acid	185	1 eq.+ . .	24	3 eq.=	209	$Ta+3O$ or TaO_3.
Terchloride .	185	1 eq.+Chlorine	106·26	3 eq.=	291·26	$Ta+3Cl$ or $TaCl_3$.
Terfluoride .	185	1 eq.+Fluorine	56·04	3 eq.=	241·04	$Ta+3F$ or TaF_3.
Sulphuret .	Composition uncertain.					

Oxide of Columbium.—It is generated by placing columbic acid in a crucible lined with charcoal, luting carefully to exclude atmospheric air, and exposing it for an hour and a half to intense heat. The acid, where in direct contact with charcoal, is entirely reduced; but the film of metal is very thin. The interior portions are pure oxide of a dark grey colour, very hard and coherent. When reduced to powder its colour is dark brown. It is not attacked by any acid, even by the nitro-hydrofluoric; but it is converted into columbic acid either by fusion with hydrate of potassa, or deflagration with nitre. When heated to low redness it takes fire and glows, yielding a light grey powder; but in this way it is never completely oxidized. Berzelius states that this oxide, in union with protoxide of iron and a little protoxide of manganese, occurs at Kimito in Finland, and may be distinguished from the other ores of columbium by yielding a chestnut-brown powder.

Its eq. is 201; symb. $Ta+2O$, $\ddot{Ta}$, or TaO_2.

Columbic Acid.—Columbium exists in most of its ores as an acid, united either with the oxides of iron and manganese, as in tantalite, or with the earth yttria, as in the yttro-tantalite. This acid is obtained by fusing its ore with three or four times its weight of carbonate of potassa, when a soluble columbate of that alkali results, from which columbic acid is precipitated as a white hydrate by acids. Berzelius also prepares it by fusion with bisulphate of potassa.

Hydrated columbic acid is tasteless, and insoluble in water; but when placed on moistened litmus paper, it communicates a red tinge. It is dissolved by the sulphuric, hydrochloric, and some vegetable acids; but it does not diminish their acidity, or appear to form definite compounds with them. With alkalies it unites readily; and though it does not neutralize their properties completely, crystallized salts may be obtained by evaporation. When the hydrated acid is heated to redness, water is expelled, and the anhydrous columbic acid remains. In this state it is attacked by alkalies only.

Its eq. is 209; symb. $Ta + 3O$, $\dddot{Ta}$, or TaO_3.

Perchloride of Columbium.—When columbium is heated in chlorine gas, it takes fire and burns actively, yielding a yellow vapour, which condenses in the cold parts of the apparatus in the form of a white powder with a tint of yellow. Its texture is not in the least crystalline. By contact with water, it is converted, with a hissing noise and increase of temperature, into columbic and hydrochloric acids. Hence its eq. is considered to be 291·26; symb. $Ta + 3Cl$, or $TaCl_3$.

Terfluoride of Columbium.—Hydrofluoric acid takes up hydrated columbic acid, and forms with it a compound of terfluoride of columbium and hydrofluoric acid, which, by evaporation at 76°, is deposited in crystals, which are soluble in water and effervesce in the air. By gently evaporating the solution, an uncrystalline mass, white and opaque, is left, which Berzelius considers to be the terfluoride of columbium. By water part of it is converted into columbic and hydrofluoric acids, the latter soluble and the former insoluble; but both of these acids retain some terfluoride in combination. Its eq. is 241·04; symb. $Ta + 3F$, or TaF_3.

Sulphuret of Columbium.—This compound, first prepared by Rose, is generated, with the phenomena of combustion, when columbium is heated to commencing redness in the vapour of sulphur; or by transmitting the vapour of bisulphuret of carbon over columbic acid in a porcelain tube at a white heat, carbonic oxide being also evolved.

SECTION XVIII.

ANTIMONY.

Hist.—First made known as a metal in the 15th century by Basil Valentine, and is said to derive its name (*anti-moine*, *anti-monk*) from having proved fatal to some monks to whom it was given as a medicine. It sometimes occurs native; but its only ore which is abundant, and from which the antimony of commerce is derived, is the sulphuret. This ore, the *stibium* of the ancients, was long regarded as the metal itself, and was called *antimony*, or *crude antimony;* while the pure metal was termed the *regulus* of *antimony*.

Prep.—Either by heating the native sulphuret in a covered crucible with half its weight of iron filings; or by mixing it with two-thirds of its weight of cream of tartar and one-third of nitre, and throwing the mixture, in small successive portions, into a red-hot crucible. By the first process the sulphur unites with iron, and in the second it is expelled in the form of sulphurous acid; while the fused antimony, which in both cases collects in the bottom of the crucible, may be drawn off and received in moulds. The antimony, thus obtained, is not absolutely pure; and therefore, for chemical purposes, should be procured by heating the oxide with an equal weight of cream of tartar.

Prop.—A brittle metal, of a white colour running into bluish-grey, and is possessed of considerable lustre. Its sp. gr. is nearly 6·7. At 810° it fuses, and on cooling acquires a highly lamellated texture, and sometimes yields crystals: like arsenic, but unlike most other metals, its primary form is a rhombohedron. It is volatile at a very intense temperature. Its surface tarnishes by exposure to the atmosphere; and by the continued action of air and moisture, a dark matter is formed, which Berzelius regards as a definite compound. It appears, however, to be merely a mixture of the sesquioxide and metallic antimony. Heated to a white or even full red heat in a covered crucible, and then suddenly exposed to the air, it inflames, and burns with a white light. During the combustion a white vapour rises, which condenses on cool surfaces, frequently in the form of small shining needles of silvery whiteness. These crystals were formerly called *argentine flowers of antimony*, and in chemical works are generally described as binoxide of antimony; but they are correctly considered by Berzelius as the sesquioxide.

From the experiments of Berzelius on the composition of the oxide and acids of antimony (An. de Ch. et Ph. xvii.), the eq. of that metal may be estimated at 64·6. The composition of its compounds described in this section is as follows:—

	2 eq. Antimony.				Equiv.	Formulæ.
Sesquioxide	129·2+	Oxygen	24	3 eq.	=153·2	$2Sb+3O$ or Sb_2O_3.
Antimonious Acid	129·2+	do.	32	4 eq.	=161·2	$2Sb+4O$ or Sb_2O_4.
Antimonic Acid	129·2+	do.	40	5 eq.	=169·2	$2Sb+5O$ or Sb_2O_5.
Sesquichloride	129·2+	Chlorine	106·26	3 eq.	=235·46	$2Sb+3Cl$ or Sb_2Cl_3.
Bichloride	129·2+	do.	141·68	4 eq.	=270·88	$2Sb+4Cl$ or Sb_2Cl_4.
Perchloride	129·2+	do.	177·1	5 eq.	=306·3	$2Sb+5Cl$ or Sb_2Cl_5.
Bromide	Composition uncertain.					
Sesquisulphuret	129·2+	Sulphur	48·3	3 eq.	=177·5	$2Sb+3S$ or Sb_2S_3.
Bisulphuret	129·2+	do.	64·4	4 eq.	=193·6	$2Sb+4S$ or Sb_2S_4.
Persulphuret	129·2+	do.	80·5	5 eq.	=209·7	$2Sb+5S$ or Sb_2S_5.
Oxychloride of Antimony		Sesquichloride	570·92	2 eq.	=1949·72	$2Sb_2Cl_3+9Sb_2O_3$.
		Sesquioxide	1378·8	9 eq.		
Oxysulphuret of Antimony		Sesquisulphuret	355	2 eq.	=508·2	$Sb_2S_3+Sb_2O_3$.
		Sesquioxide	153·2	1 eq.		

Sesquioxide.—When sesquichloride of antimony, made by boiling the native sulphuret in hydrochloric acid, is poured into water, a white curdy precipitate subsides, formerly called *powder of Algaroth*, which consists of sesquioxide of antimony combined with undecomposed chloride. On decomposing the latter by digestion with carbonate of potassa, and then washing with water, the sesquioxide is obtained in a state of purity. It may also be procured by adding carbonate of potassa or soda to a solution of tartar emetic, and by sublimation during the combustion of antimony. When slowly sublimed it condenses in fine needles of silvery whiteness. It occurs as a mineral, the oxide of antimony of mineralogists, the primary form of which is a right rhombic prism, isomorphous with the crystals of arsenious acid lately observed by Wöhler.

Prop.—When prepared in the moist way, it is a white powder with a somewhat dirty appearance. When heated it acquires a yellow tint, and at a dull red heat in close vessels it is fused, yielding a yellow fluid, which becomes an opaque greyish crystalline mass on cooling. Its sp. gr. is 5·566. It is very volatile, and if protected from atmospheric air may be sublimed without change. When heated in open vessels it absorbs oxygen; and when the temperature is suddenly raised, and the oxide is porous, it takes fire and burns. In both cases antimonious acid is generated. It is the only oxide of antimony which forms regular salts with acids, and is the base of the medicinal preparation *tartar emetic*, the tartrate of antimony and potash. Most of its salts, however, are either insoluble in water, or, like chloride of antimony, are decomposed by it, owing to the affinity of that fluid for the acid being greater than that of the acid for oxide of antimony. This oxide is therefore a feeble base; and, indeed, possesses the property of uniting with alkalies. To the foregoing remark, however, tartrate of antimony and potassa is an exception; for it dissolves readily in water without change. By excess of tartaric or hydrochloric acid, the insoluble salts of antimony may be rendered soluble in water.

The presence of antimony in solution is easily detected by hydrosulphuric acid. This gas occasions an orange-coloured precipitate, hydrated sesquisulphuret of antimony, which is soluble in pure potassa, and is dissolved with disengagement of hydrosulphuric acid gas by hot hydrochloric acid, forming a solution from which the white oxychloride is precipitated by water.

In trying the effect of reagents on solutions of oxide of antimony, it is convenient to employ tartar emetic, from its property of dissolving in pure water without decomposition. From a solution of this salt, when moderately concentrated, a little pure potassa throws down the oxide, but excess of the alkali redissolves the precipitate. The oxide is more perfectly separated by alkaline carbonates. Lime water causes a white precipitate, a mixed tartrate of lime and oxide of antimony; and earthy and metallic salts decompose tartar emetic by forming, like lime, sparingly soluble compounds with tartaric acid. Decomposition is also occasioned by most acids, which throw down a sparingly soluble salt of antimony and cream of tartar; and a recently made, pretty strong, infusion of gall-nuts gives a yellowish white precipitate, which consists of tannic acid and oxide of antimony. But these appearances are by no means to be relied on as tests of the presence of antimony: a mixture of other substances might be similarly influenced by the same reagents; in a moderately dilute solution of tartar emetic most of them produce no effect whatever; and the too free addition of a pure alkali or of an acid, even to a strong solution, may altogether prevent that precipitate from forming, which a smaller quantity of the same reagents would have produced. The only certain method of bringing the antimony into view, even in a very weak solution, is to acidulate with tartaric acid, and then transmit through the liquid a current of hydrosulphuric acid gas. The hydrated sesquisulphuret of antimony, of a characteristic orange-red colour, is immediately formed.

The detection of antimony in mixed fluids, as when tartar emetic is mixed with articles of food, is conducted in the following manner. The substances are first digested in water acidulated with about a drachm of hydrochloric and tartaric acids, which coagulate some organic matters, and give complete solubility to the oxide of antimony. Through the filtered liquid, hydrosulphuric acid is then transmitted, when the orange-red sesquisulphuret of antimony subsides, which preserves its characteristic tint even when deposited from coloured solutions, and may be further recognized by solution in hot hydrochloric acid and precipitation by water. The metal itself may in general be obtained by placing the dry sulphuret in a glass tube, transmitting through it a current of hydrogen gas, and then, when all the atmospheric air is displaced, heating the sulphuret by the flame of a spirit-lamp. The sulphur is carried off in the form of hydrosulphuric acid gas, and the metallic antimony, recognizable by its lustre, remains. The metal is principally found where the sulphuret lay; but if the current of gas during the reduction happen to be rapid, it causes mechanically a spurious sublimation of antimony, which lines part of the tube with a thin film of metal. When much organic matter is mixed with the sulphuret, the metal is sometimes indistinctly seen. In that case it should be dissolved in a few drops of nitro-hydrochloric acid with heat, and be precipitated by water: it may then be redissolved by tartaric acid, and again precipitated with its characteristic tint by hydrosulphuric acid. Orfila recommends that the metal should be obtained from the sulphuret by fusion with black flux; but I have elsewhere shown this process to be very precarious, and my opinion is supported by the experience of Christison. (Treatise on Poisons, 2nd Ed. 429.) It may be detected, when present even in small quantity, by decomposing the antimoniuretted hydrogen formed as described under Arsenic, where the characters by which it is distinguished from arsenic are given.

Its eq. is 153·2; symb. $2Sb + 3O$, $\underline{\overset{\cdots}{Sb}}$, or Sb_2O_3.

Antimonious Acid.—When metallic antimony is digested in strong nitric acid, the metal is oxidized at the expense of the acid, and hydrated antimonic acid is formed; and on exposing this substance to a red heat, it gives out water and oxygen gas, and is converted into antimonious acid. It is also generated when the oxide is exposed to heat in open vessels. Thus, on heating sulphuret of antimony with free exposure to the air, sulphurous acid and oxide of antimony are generated; but on continuing the roasting after all the sulphur is burned, the oxide gradually absorbs oxygen and passes into antimonious acid. Hence this acid is formed in the process of preparing the *pulvis antimonialis* of the pharmacopœia. Antimonious acid is white while cold, but acquires a yellow tint when heated, is very infusible, and fixed in the fire, two characters by which it is readily distinguished from the oxide. It is insoluble in water, and likewise in acids after being heated to redness. It combines in definite proportions with alkalies, and its salts are called *antimonites.* Antimonious acid is precipitated from these salts by acids as a hydrate, which reddens litmus paper, and is dissolved by hydrochloric and tartaric acids, though without appearing to form with them definite compounds.

Its eq. is 161·2; symb. $2Sb + 4O$, $\overset{\cdot\cdot\cdot\cdot}{\underline{Sb}}$, or Sb_2O_4.

Antimonic Acid, sometimes called *peroxide* of antimony, is obtained as a white hydrate, either by digesting the metal in strong nitric acid, or by dissolving it in nitro-hydrochloric acid, concentrating by heat to expel excess of acid, and throwing the solution into water. When recently precipitated it reddens litmus paper, and may then be dissolved in water by means of hydrochloric or tartaric acid. It does not enter into definite combination with acids, but with alkalies forms salts, which are called *antimoniates.* When the hydrated peroxide is exposed to a temperature of 500° or 600° F. the water is evolved, and the anhydrous acid of a yellow colour remains. In this state it resists the action of acids. When exposed to a red heat, it parts with oxygen, and is converted into antimonious acid.

Its eq. is 169·2; symb. $2Sb + 5O$, $\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{Sb}}$, or Sb_2O_5.

Chlorides of Antimony.—When antimony in powder is thrown into a jar of chlorine gas, combustion ensues, and the sesquichloride of antimony is generated. The same compound may be formed by distilling a mixture of antimony with about twice and a half its weight of corrosive sublimate, when the volatile sesquichloride of antimony passes over into the recipient, and metallic mercury remains in the retort. At common temperatures it is a soft solid, thence called *butter of antimony*, which is liquefied by gentle heat, and crystallizes on cooling. It deliquesces on exposure to the air; and when mixed with water, hydrochloric acid and sesquioxide are generated, and the latter, combined with undecomposed chloride, subsides.

Its eq. is 235·46; symb. $2Sb + 3Cl$, or Sb_2Cl_3.

The *bichloride of antimony* is formed by acting on hydrated antimonious by hydrochloric acid, when a solution is formed, which appears to be a compound of bichloride of antimony and hydrochloric acid. It possesses little permanence, and on the addition of water antimonious acid subsides, and hydrochloric acid remains in solution.

The *perchloride* is generated by passing dry chlorine gas over heated metallic antimony. It is a transparent volatile liquid, which emits fumes on exposure to the air. Mixed with water, it is converted into hydrochloric and hydrated antimonic acid, which subsides. (Rose, in the Annals of Philosophy, N. S. x.)

Bromide of Antimony.—The union of bromine and antimony is attended with disengagement of heat and light, and the compound is readily obtained by distillation, as in the process for preparing bromide of arsenic. It is solid at common temperatures, is fused at 206°, and boils at 518° F. It is colourless, and crystallizes in needles; it attracts moisture from the air, and is decomposed by water.

Sesquisulphuret of Antimony.—This is by far the most abundant ore of antimony, and is hence employed in making the preparations of antimony. Though compact or earthy, it sometimes occurs in acicular crystals and in rhombic prisms. Its sp. gr. is 4·62, colour red-grey, and its lustre metallic. When heated in close vessels, it enters into fusion without undergoing any other change. It may be formed artificially by fusing together antimony and sulphur, or by transmitting a current of hydrosulphuric acid gas through a solution of tartar emetic: in this case it falls as a hydrate of an orange-red colour, and does not acquire its dark colour till its water is expelled by heat.

Its eq. is 177·5; symb. $2Sb + 3S$, or Sb_2S_3.

The *bisulphuret* is formed, according to Rose, by transmitting hydrosulphuric acid gas through a solution of antimonious acid in dilute hydrochloric acid. (An. of Phil. N. S. x.)

Its eq. is 193·6; symb. $2Sb + 4S$, or Sb_2S_4.

Rose formed the *persulphuret* by the action of hydrosulphuric acid on a solution of antimonic acid. The golden sulphuret, prepared by boiling sulphuret of antimony and sulphur in solution of potassa, a process which is not adopted by either of our colleges, is a persulphuret. Its eq. 209·7; symb. $2Sb + 5S$, or Sb_2S_5.

Oxychloride of Antimony.— This compound has lately been studied by Malaguti and Johnston. When an acid solution of the sesquichloride of antimony is thrown into a large quantity of water, a white voluminous precipitate forms. Allowing it to subside, it contracts considerably during thirty or forty hours, and then consists of a thick bed of minute crystals. These crystals are small prismatic needles, of a white colour and brilliant lustre; they are decomposed by boiling in water, by continued washings, and by the alkaline carbonates, being thus converted into sesquioxide. They have been analyzed by Johnston, according to whom they are composed of 2 eq. of the sesquichloride united with 9 eq. of the sesquioxide; a composition which corresponds closely with the analysis of Malaguti. Hence the eq. is 1949·72; symb. $2Sb_2Cl_3 + 9Sb_2O_3$.

Oxysulphuret of Antimony.— Hist. and Prep.— Rose has shown that this compound occurs in the mineral kingdom, being the *red antimony ore* (rothspiesglanzerz) of mineralogists. The pharmaceutic preparations known by the terms *glass*, *liver*, and *crocus* of antimony, are of a similar nature, though less definite in composition. They are made by roasting the native sulphuret, so as to form sulphurous acid and oxide of antimony, and then vitrifying the oxide together with undecomposed ore, by means of a strong heat. The product will of course differ according as more or less of the sulphuret escapes oxidation during the process.

When sulphuret of antimony is boiled in a solution of potassa or soda, a liquid is obtained, from which on cooling an orange-red matter called *Kermes mineral* is deposited; and on subsequently neutralizing the cold solution with an acid, an additional quantity of a similar substance, the *golden sulphuret* of the pharmacopœia, subsides. These compounds may also be obtained by igniting sulphuret of antimony with an alkali or alkaline carbonate, and treating the product with hot water; or by boiling the mineral in a solution of carbonate of soda or potassa. The finest kermes is obtained, according to M. Cluzel, from a mixture of four parts of sulphuret of antimony, 90 of crystallized carbonate of soda, and 1000 of water. These materials are boiled for half or three quarters of an hour; the hot solution is filtered into a warm vessel, in order that it may cool slowly; and after 24 hours the deposit is collected on a filter, moderately washed with cold water, and dried at a temperature of 70° or 80° F.

Prop.—Very great diversity of opinion has long existed among chemists as to the nature of kermes. Berzelius and Rose gave experiments to show that it is a hydrated sesquisulphuret, differing from the native sulphuret solely in being combined with water. Subsequently Gay-Lussac and others observed that kermes contains oxide of antimony, which may be removed by digestion with cream of tartar; and Gay-Lussac inferred from the quantity of water formed when kermes, previously rendered anhydrous, is reduced by hydrogen gas, that it is a hydrated oxysulphuret, identical, when deprived of its water, with the red ore of antimony above referred to. Still more recently Berzelius has explained, that the ordinary process for making kermes leads to the separation of a compound of oxide of antimony and potassa, which tenaciously adheres to kermes, but is not chemically united with it: he rightly argues that the question is not, whether oxide of antimony is sometimes or generally present in kermes, but whether the latter can exist *without* oxide of antimony. This question he has answered affirmatively. He fused sulphuret of antimony with black flux, boiled the residue in water, and set aside the solution to cool: a perfect kermes was deposited, which he considers, and I apprehend with good reason, to be quite free from oxide of antimony. (Pog. Annalen, xx. 364.)

The theory of the preparation of kermes, as given by Berzelius, is the following. When sesquisulphuret of antimony is fused with potassa, part of each interchanges elements with the other in such a ratio that

1 eq. Sesquisulphuret of Ant.	Sb_2S_3	yield	1 eq. Sesquioxide of Antimony	Sb_2O_3
and 3 eq. Potassa	$3KO$		and 3 eq. Sulphuret of Potassium	$3KS$.

The sulphuret of potassium unites with undecomposed sesquisulphuret of antimony, forming a sulphur-salt which will be again referred to hereafter, and sesquioxide of antimony with undecomposed potassa; and on adding hot water both compounds are dissolved, and coexist independently of each other in the solution. As the solution cools, the sesquisulphuret of antimony subsides, simply because the solvent power of sulphuret of potassium is thereby diminished; but a variable quantity of potassa and sesquioxide of antimony falls with the deposit, and cannot be entirely removed by washing with water. The cold solution still contains a double sulphuret of antimony and potassium, together with sesquioxide of antimony united with potassa: on acidulating with sulphuric acid, the sulphuret of potassium is resolved, by decomposition of water, into potassa and hydrosulphuric acid, and the sesquioxide of antimony is deprived of its potassa; and therefore the sesquisulphuret and sesquioxide of antimony, both losing at the same instant the principles which gave them solubility, are thrown down either in combination or in mixture with each other. Berzelius believes the same change to occur when the ingredients are boiled instead of fused together. The golden sulphuret differs from kermes, in the absence of potassa, in containing more oxide of antimony, and perhaps in being or containing an oxysulphuret. It commonly contains free sulphur, derived apparently from the oxidizing influence of the air on the sulphuret of potassium. When alkaline carbonates are employed instead of pure alkalies, the same phenomena ensue, except that carbonic acid is evolved.

Its eq. is 508·2; symb. $2Sb_2S_3+Sb_2O_3$.

SECTION XIX.

URANIUM.—CERIUM.—LANTANIUM.

URANIUM.

Hist. and Prep.—This metal was discovered in 1789 by the German analyst Klaproth, who named it after the new planet Uranus, the discovery of which took place in the same year. It was obtained from a mineral of Saxony, called from its black colour *pitchblende*, which consists of protoxide of uranium and oxide of iron. From this ore the uranium may be conveniently extracted by the following process. After heating the mineral to redness, and reducing it to fine powder, it is digested in pure nitric acid diluted with three or four parts of water, taking the precaution to employ a larger quantity of the mineral than the nitric acid present can dissolve. By this mode of operating, the protoxide is converted into peroxide of uranium, which unites with the nitric acid almost to the total exclusion of the iron. A current of hydrosulphuric acid gas is then transmitted through the solution, in order to separate lead and copper, the sulphurets of which are always mixed with pitchblende. The solution is boiled to expel free hydrosulphuric acid, and after being concentrated by evaporation, is set aside to crystallize. The nitrate of peroxide of uranium is gradually deposited in flattened four-sided prisms of a beautiful lemon-yellow colour.

Prop.—The properties of metallic uranium are as yet known imperfectly. It was prepared by Arfwedson by conducting hydrogen gas over the protoxide of uranium heated in a glass tube. The substance obtained by this process was crystalline, of a metallic lustre, and of a reddish-brown colour. It suffered no change on exposure to air at common temperatures; but when heated in open vessels, it absorbed oxygen, and was reconverted into the protoxide. From its lustre it was inferred to be metallic uranium.

From the experiments of Arfwedson and Berzelius on the oxides of uranium, the eq. of the metal may be estimated at 217. (An. of Ph. N. S. vii. 258); its symb. is U. Its compounds described in this section are thus constituted:—

	Uranium.			Equiv.	Formulæ.
Protoxide	217	1 eq.+Oxygen	8	1 eq.=225	$U+O$ or UO.
Peroxide	434	2 eq.+do.	24	3 eq.=458	$2U+3O$ or U_2O_3.
Protochloride	217	1 eq.+Chlorine	35·42	1 eq.=252·42	$U+Cl$ or UCl.
Perchloride	434	2 eq.+do.	106·26	3 eq.=540·26	$2U+3Cl$ or U_2Cl_3.
Sulphuret.	Composition unknown.				

Protoxide.—This oxide is of a very dark green colour, and is obtained by exposing nitrate of the peroxide to a strong heat. It is exceedingly infusible, and bears any temperature hitherto tried without change. It unites with acids, forming salts of a green colour. It is readily oxidized by nitric acid, yielding a nitrate of the peroxide. The protoxide is employed in the arts by giving a black colour to porcelain.

Its eq. is 225; symb. $U + O$, $\dot{U}$, or UO.

Peroxide of Uranium is of a yellow or orange colour, and most of its salts have a similar tint. It not only combines with acids, but likewise unites with alkaline bases, a property which was first noticed by Arfwedson. It is precipitated from acids as a yellow hydrate by pure alkalies, fixed or volatile; but retains a portion of these bases in combination. It is thrown down as a carbonate by alkaline carbonates, but is redissolved by an excess of carbonate of soda or ammonia, a circumstance which affords an easy method of separating uranium from iron. It is not precipitated by hydrosulphuric acid, but acquires a green tint from partial deoxidation. With ferrocyanuret of potassium it gives a brownish-red precipitate, very like ferrocyanuret of copper.

Peroxide of uranium is decomposed by a strong heat, and converted into the protoxide. From its affinity for alkalies, it is difficult to obtain it in a state of perfect purity. It is employed in the arts for giving an orange colour to porcelain.

Its eq. is 458 ; symb. $2U + 3O$, $\underline{\dddot{U}}$, or U_2O_3.

Chlorides.—These compounds are obtained in solution by dissolving the corresponding oxides in hydrochloric acid. The protochloride is green, very soluble, and does not crystallize. The perchloride is yellow, deliquescent, soluble in alcohol, ether, and water, and yields yellow solutions.

Sulphuret of Uranium may be formed by transmitting the vapour of bisulphuret of carbon over protoxide of uranium strongly heated in a tube of porcelain. (Rose.) It is of a dark-grey or nearly black colour, is converted into protoxide of uranium when heated in the open air, and is readily dissolved by nitric acid. Hydrochloric acid attacks it feebly.

CERIUM.—LANTANIUM.

Cerium, named after the planet Ceres, was discovered in the year 1803 by Hisinger and Berzelius, in a rare Swedish mineral known by the name of Cerite, and its existence was recognized about the same time by Klaproth. Thomson has since found it to the extent of thirty-four per cent. in a mineral from Greenland, called *Allanite*, in honour of the late Mr. Allan, who first distinguished it as a distinct species.

Very lately, Mosander has shown that the oxide commonly considered as oxide of cerium contains a large proportion of the oxide of a new metal, to which he has given the name of Lantanium (from λανθανω, *I lurk*, it having lain concealed in the ores of cerium). The properties and compounds of this new metal have not yet been fully investigated, and of course those of pure cerium are equally unknown. There is, however, a great analogy between them, each forming two oxides, both of which unite with acids. The carbonates of both protoxides are white and insoluble; the sulphates soluble and crystallizable.

By the following process the two oxides may be conveniently separated. The mixed oxide is dissolved in nitric acid, the solution evaporated to dryness, and the residue calcined. The oxide is now powdered, and digested in weak nitric acid (1 of acid to

50 or 100 of water), which dissolves the oxide of lantanium, and leaves the oxide of cerium undissolved. The former may be precipitated as carbonate by a carbonated alkali; the latter may be dissolved by a strong acid, and also converted into carbonate. It would be absurd, in the present state of our knowledge, to give details as to the compounds of these two metals, which cannot possibly be correct.

The symbol of cerium is Ce; that of lantanium will be La. Both metals are more closely allied to yttrium and zirconium than to any others.

SECTION XX.

BISMUTH.—TITANIUM.—TELLURIUM.

BISMUTH.

Hist. and Prep.—This metal was known to the ancients, though often confounded by them with lead and tin; but it appears to have derived the name of *bismuth*, or properly *wismuth*, from the German miners. It occurs in the earth both native and in combination with other substances, such as sulphur, oxygen, and arsenic. That which is employed in the arts is derived chiefly from native bismuth, and commonly contains small quantites of sulphur, iron, and copper. It may be obtained pure for chemical purposes by heating the oxide or subnitrate to redness along with charcoal.

Prop.—Bismuth has a reddish-white colour and considerable lustre. Its structure is highly lamellated, and when slowly cooled it crystallizes in cubes or octohedrons. Its density is about 10. It is brittle when cold, but may be hammered into plates while warm. At 476° it fuses, and sublimes in close vessels at a red heat. It is a less perfect conductor of heat than most other metals.

Bismuth undergoes little change by exposure to air at common temperatures. When fused in open vessels, its surface becomes covered with a grey film, which is a mixture of metallic bismuth with the oxide of the metal. Heated to its subliming point, it burns with a bluish-white flame, and emits copious fumes of oxide of bismuth. The metal is attacked with difficulty by hydrochloric or sulphuric acid, but it is readily oxidized and dissolved by nitric acid.

The eq. of bismuth, deduced by Lagerhjelm from the composition of its protoxide, is 71 (An. of Phil. iv. 357); its symb. is Bi. Its compounds described in this section are thus constituted:—

	Bismuth.				Equiv.	Formulæ.
Protoxide	71	1 eq.+	Oxygen	8	1 eq.= 79	$Bi+O$ or BiO.
Peroxide	142	2 eq.+	do.	24	3 eq.=166	$2Bi+3O$ or Bi_2O_3.
Chloride	71	1 eq.+	Chlorine	35·42	1 eq.=106·42	$Bi+Cl$ or $BiCl$.
Bromide	71	1 eq.+	Bromine	78·4	1 eq.=149·4	$Bi+Br$ or $BiBr$.
Sulphuret	71	1 eq.+	Sulphur	16·1	1 eq.= 87·1	$Bi+S$ or BiS.

Protoxide of Bismuth.—This compound is readily prepared by heating to redness the nitrate or subnitrate of oxide of bismuth. Its colour is yellow; at a full red heat it is fused into a brown liquid, which on cooling becomes a yellow transparent glass of sp. gr. 8·211. At intense temperatures it is sublimed. It unites with acids, and most of its salts are white.

When nitrate of oxide of bismuth, either in solution or in crystals, is put into water, a copious precipitate, the subnitrate, of a beautifully white colour, subsides, which was formerly called the *magistery of bismuth.* From its whiteness it is sometimes employed as a paint for improving the complexion; but it is an inconvenient cosmetic, owing to the facility with which it is blackened by hydrosulphuric acid. If the nitrate with which it is made contains no excess of acid, and a large quantity of water is employed, nearly the whole of the bismuth is separated as a subnitrate.—By this character bismuth may be both distinguished and separated from other metals.

Its eq. is 79; symb. $Bi+O$, $\dot{Bi}$, or BiO.

Peroxide.—This oxide was first noticed by Bucholz and Brandes, but its nature and composition have been recently examined by A. Stromeyer. It is generated when hydrate of potassa is fused at a moderate heat with protoxide of bismuth; but the best mode of preparation is first to prepare the protoxide by igniting the subnitrate, and then gently heating it for some time in a solution of chloride of potassa or soda. After washing with water, any unchanged protoxide is dissolved by a solution made with 1 part of nitric acid (quite free from nitrous acid) and 9 of water.

As thus prepared, peroxide of bismuth is a heavy powder of a brown colour, very like peroxide of lead, manifests little disposition to unite either with acids or alkalies, and is reconverted by heat with loss of oxygen into the protoxide. Heated with sulphuric or phosphoric acid, it gives off oxygen gas, and a sulphate or phosphate of the protoxide is formed; and with hydrochloric acid chlorine is evolved, and the protochloride produced (An. de Ch. et Ph. li. 267). Its eq. is 166; symb. $2\mathrm{Bi}+3\mathrm{O}$, $\overset{\cdots}{\underline{\mathrm{Bi}}}$, or $\mathrm{Bi}_2\mathrm{O}_3$.

Chloride of Bismuth.—When bismuth in fine powder is introduced into chlorine gas, it takes fire, burns with a pale blue light, and is converted into a chloride, formerly termed *butter* of bismuth. It may be prepared conveniently by heating two parts of corrosive sublimate with one of bismuth, and afterwards expelling the excess of the former, together with the metallic mercury, by heat.

Chloride of bismuth is of a greyish-white colour, opaque, and of a granular texture. It fuses at a temperature a little above that at which the metal itself is liquefied, and bears a red heat in close vessels without subliming.

Its eq. is 106·42; symb. $\mathrm{Bi}+\mathrm{Cl}$, or BiCl.

Bromide of Bismuth is prepared by heating the metal with a large excess of bromine in a long tube; when a grey-coloured bromide results, similar in its aspect to fused iodine. At 392° it enters into fusion, and at a low red heat sublimes. With water it is converted into oxide of bismuth and hydrobromic acid, the former of which combines with some undecomposed bromide of bismuth as an oxybromide. (Serullas.)

Its eq. is 149·4; symb. $\mathrm{Bi}+\mathrm{Br}$, or BiBr.

Sulphuret of Bismuth.—This sulphuret is found native, and may be formed artificially by fusing bismuth with sulphur, or by the action of hydrosulphuric acid on the salts of bismuth. It is of a lead-grey colour and metallic lustre.

Its eq. is 87·1; symb. $\mathrm{Bi}+\mathrm{S}$, or BiS.

TITANIUM.

Hist.—This metal was first recognized as a new substance by Mr. Gregor of Cornwall, and its existence was afterwards established by Klaproth, who fancifully gave it the name of *Titanium*, after the *Titans* of ancient fable. (Contributions, i.) But the properties of the metal were not ascertained in a satisfactory manner until the year 1822, when Wollaston was led to examine some minute crystals which were found in a slag at the bottom of a smelting furnace at the great iron works at Merthyr Tydvil in Wales, and presented to him by Buckland. (Philosophical Transactions, 1823.) These crystals, which have since been found at other iron works, are of a cubic form, and in colour and lustre resemble burnished copper. They are found in the blast furnaces, and are probably derived principally from the hearth-stone, which contains them abundantly. They conduct electricity, and are attracted slightly by the magnet, a property which seems owing to the presence of a minute quantity of iron. Their sp. gr. is 5·3; and their hardness is so great, that they scratch a polished surface of rock crystal. They are exceedingly infusible; but when exposed to the united action of heat and air, their surface becomes covered with a purple-coloured film, which is an oxide. They resist the action of nitric and nitro-hydrochloric acids, but are completely oxidized by being strongly heated with nitre. They are then converted into a white substance, which possesses all the properties of titanic acid.

Prep.—Liebig prepares metallic titanium by putting fragments of recently made chloride of titanium and ammonia into a glass tube half an inch wide and two or three feet long, transmitting through it a current of perfectly dry ammonia, and when atmospheric air is entirely displaced, applying heat until the glass softens. Complete decomposition ensues, nitrogen gas is disengaged, hydrochlorate of ammonia sublimes, and metallic titanium is left in the state of a deep blue-coloured powder. If exposed to the air while warm, it is apt to take fire.

The eq. of titanium, determined by Rose from his analysis of the bichloride, is 24·3; its symb. is Ti. The composition of its compounds described in this section is as follows:—

	1 eq. Titanium.		Equiv.	Formulæ.
Oxide (probably)	24·3+Oxygen	8	1 eq.=32·3	$Ti+O$ or TiO.
Titanic Acid .	24·3+do.	16	2 eq.=40·3	$Ti+2O$ or TiO_2.
Bichloride .	24·3+Chlorine	70·84	2 eq.=95·14	$Ti+2Cl$ or $TiCl_2$.
Bisulphuret .	24·3+Sulphur	32·2	2 eq.=56·5	$Ti+2S$ or TiS_2.

Oxide of Titanium.—When titanic is exposed to a strong heat in a black-lead crucible, a mass is obtained, the exterior crust of which is metallic titanium, but the interior parts consist of the supposed protoxide. As thus prepared it is a black mass, which has an earthy fracture, is quite insoluble in all acids, and is very difficult to oxidize. Oxide of titanium is formed in the moist way, when a fragment of zinc or iron is introduced into a solution of titanic acid in hydrochloric acid. The solution soon acquires a purple tint, and after a time the whole of the titanic acid is thrown down in the form of a deep purple powder. This cannot be collected, owing to the facility with which it is reconverted into titanic acid; hence its composition and chemical properties are unknown.

Titanic Acid.—Hist. and Prep.—This compound, called also peroxide of titanium, has been carefully studied by H. Rose, who first pointed out its acid properties. It occurs in a nearly pure state in the minerals rutile and anatase, which are remarkable for presenting the same chemical compound crystallized in unconnected forms. It also exists in titanite or sphene as titanate and silicate of lime, and menaccanite as titanate of the oxides of iron and manganese, in the latter of which titanium was originally discovered by Gregor. It is best prepared from rutile. The mineral, after being reduced to an exceedingly fine powder, is fused in a platinum crucible with three times its weight of carbonate of potash, and the mass afterwards washed with water to remove the excess of alkali. A grey mass remains, which consists of potash and titanic acid. This compound is dissolved in concentrated hydrochloric acid; and on diluting with water, and boiling the solution, the greater part of the titanic acid is thrown down. It is then collected on a filter, and well washed with water acidulated with hydrochloric acid. In this state it is not quite pure; but contains a little oxide of manganese and iron, derived from the rutile. The best mode of separating these impurities is to digest the precipitate, while still moist, with hydrosulphate of ammonia, which converts the oxides of iron and manganese into sulphurets, but does not act on the titanic acid. The two sulphurets are readily dissolved by dilute hydrochloric acid; and the titanic acid, after being collected on a filter and well washed as before, may be dried and heated to redness. This method, proposed by Rose of Berlin, has been thus simplified by himself. Either rutile or titaniferous iron, after being pulverized and washed, is exposed in a porcelain tube at a very strong red heat to a current of hydrosulphuric acid gas, which acts upon the oxide of iron, giving rise to water and sulphuret of iron. As soon as water ceases to appear, the process is discontinued, the mass digested in hydrochloric acid to remove the iron, and the titanic acid separated from adhering sulphur by heat. A little iron is still usually retained; but the whole may be removed by a repetition of the same process. (An. de Ch. et Ph. xxiii. and xxxviii. 131.)

Prop.—Titanic acid, when pure, is quite white. It is exceedingly infusible; and after being once ignited it ceases to be soluble in acids, except in the hydrofluoric. In its chemical relations it is analogous to silicic acid, being a feeble acid, insoluble in water, without action on test paper, but combining with metallic oxides. In the state of hydrate, as when precipitated from hydrochloric acid by boiling, or when combined with an alkali after fusion, it has a singular tendency to pass through the pores of a filter when washed with pure water; but the presence of a little acid, alkali, or salt, prevents this inconvenience.

If previously ignited with carbonate of potassa, titanic acid is soluble in dilute hydrochloric acid; but it is retained in solution by so feeble an attraction, that it is precipitated merely by boiling. It is likewise thrown drown by the pure and carbonated alkalies, both fixed and volatile. A solution of gall-nuts causes an orange-red colour, which is very characteristic of titanic acid; an effect which appears owing to tannic, and not to gallic acid. When a rod of zinc is suspended in the solution, a purple-coloured powder, probably the protoxide, is precipitated, which is gradually converted into titanic acid. Its eq. is 40·3; symb. $Ti + 2O$, $\ddot{\mathrm{T}}\mathrm{i}$, or TiO_2.

Bichloride of Titanium.—This substance was discovered in the year 1824 by Mr. George of Leeds, by transmitting dry chlorine gas over metallic titanium at a red heat. Rose prepared it for his analysis by heating a mixture of titanic acid and charcoal in a tube, through which dry chlorine gas was passing: the resulting bichloride was purified from adhering free chlorine by agitation either with mercury or potassium, and repeated distillation. At common temperatures it is a transparent colourless fluid, of considerable sp. gr., boils violently at a temperature a little above 212°, and condenses again without change. Dumas has shown that the density of its vapour may be estimated at 6·615. In open vessels it is attacked by the moisture of the atmosphere, and emits dense white fumes of a pungent odour similar to that of chlorine, but not so offensive. On adding a few drops of water to a few drops of the liquid, combination ensues with almost explosive violence, from the evolution of intense heat; and if the water is not in excess, a solid hydrate is obtained. On exposure to the air it deliquesces, and on adding water the greater part is dissolved. The bichloride, when exposed to an atmosphere of dry ammonia, absorbs a large quantity of the gas, and becomes solid. It was from this compound Liebig prepared metallic titanium.

Its eq. is 95·14; symb. $Ti + 2Cl$, or $TiCl_2$.

Bisulphuret of Titanium.—This compound was discovered by Rose, who prepared it by transmitting the vapour of bisulphuret of carbon over titanic acid, heated to whiteness in a tube of porcelain. It occurs in thick green masses, which by the least friction acquire a dark yellow colour and metallic lustre. When heated in the open air it is converted into sulphurous and titanic acids. By acids it is slowly decomposed, and is dissolved by hydrochloric acid with disengagement of hydrosulphuric acid gas.

Its eq. is 56·5 : symb. $Ti + 2S$, or TiS_2.

TELLURIUM.

Hist.—A rare metal, hitherto found only in the gold mines of Transylvania, and even there in very small quantity. Its existence was inferred by Müller in the year 1782, and fully established in 1798 by Klaproth, who gave it the name of *tellurium*, from *tellus, the earth*, suggested by the source from which he drew the name of uranium. (Contributions, iii.) It occurs in the metallic state, chiefly in combination with gold and silver.

Prop.—It has a tin-white colour running into lead-grey, a strong metallic lustre, and lamellated texture. It is very brittle, and its density is 6·2578. It fuses at a temperature below redness, and at a red heat is volatile. When heated before the blowpipe, it takes fire, burns rapidly with a blue flame bordered with green, and is dissipated in grey-coloured pungent inodorous fumes. The odour of decayed horse-radish is sometimes emitted during the combustion, and was thought by Klaproth to be peculiar to tellurium; but Berzelius ascribes it solely to the presence of selenium.

From some experiments of Berzelius the eq. of tellurium is 64·2; its symb. is Te. The compounds described in this section are thus constituted :—

	1 eq. Tellurium.			Equiv.	Formulæ.
Tellurous Acid	64·2 + Oxygen .	16	2 eq. =	80·2	$Te+2O$ or TeO_2.
Telluric Acid .	64·2 + . . .	24	3 eq. =	88·2	$Te+3O$ or TeO_3.
Chloride . .	64·2 + Chlorine .	35·42	1 eq. =	99·62	$Te+Cl$ or $TeCl$.
Bichloride .	64·2 + . . .	70·84	2 eq. =	135·04	$Te+2Cl$ or $TeCl_2$.
Bisulphuret .	64·2 + Sulphur .	32·2	2 eq. =	96·4	$Te+2S$ or TeS_2.
Persulphuret .	Composition uncertain.				
Hydrotelluric Acid	64·2 + Hydrogen	1	1 eq. =	65·2	$Te+H$ or TeH.

Tellurous Acid.—This compound, also called *oxide of tellurium*, is generated by the action of nitric acid on tellurium, by which acid it is dissolved; but the solution possesses such little permanence that mere effusion of water precipitates part of it, and the rest is obtained by evaporating to dryness. In this state it is a white granular anhydrous powder, which slowly reddens moist litmus paper, and is insoluble in water and acids. By pure potassa or soda in solution it is dissolved, and is rendered soluble by fusion with the alkaline carbonates, forming with those alkalies crystallizable salts. Acids added in slight excess to the alkaline solutions throw down tellurous acid as a white flaky hydrate, which if washed in ice-cold water, and dried at a temperature not exceeding 53°, may be preserved unchanged. In this state it is freely soluble in acids, in ammonia, in the alkaline carbonates, from which it expels carbonic acid, and even to considerable extent in pure water. Its aqueous solution reddens litmus paper: it becomes turbid at 68°, and the acid which falls is no longer soluble in acids. In these properties tellurous acid closely resembles the titanic and several other feeble acids, which have a soluble hydrated state easily convertible into an insoluble anhydrous one. Its salts are precipitated black by hydrosulphuric acid, bisulphuret of tellurium being formed. It is deoxidized and metallic tellurium falls as a black powder, when a piece of zinc, tin, iron, or antimony is left in its solution. Its eq. is 80·2; symb. $Te + 2O$, $\ddot{T}e$, or TeO_2.

Telluric Acid.—The process which Berzelius recommends for preparing this compound is either to deflagrate tellurous acid with nitre, or to mix pure potassa freely with a solution of tellurite of potassa, and to saturate fully with chlorine. Nitric acid in slight excess and a little chloride of barium are added, in order to precipitate any traces of sulphuric and selenic acids; and after separating the precipitate by filtration, the liquid is exactly neutralized with ammonia, and chloride of barium added as long as it causes a precipitate. The tellurate of baryta is washed, dried by a gentle heat, and then digested with a fourth of its weight of strong sulphuric acid previously diluted with water: the filtered solution is then concentrated by a water bath, and on cooling or subsequent spontaneous evaporation yields hydrated telluric acid in the form of flat six-sided prisms. Adhering sulphuric acid is removed by alcohol.

This hydrate consists of 1 eq. of acid and 3 eq. of water. When heated at 212° it loses two of its eq. of water; and on heating still further all its water is expelled, and the anhydrous acid of a lemon-yellow colour remains. In this state it is insoluble in all fluids, whereas the hydrated acid is soluble in water; and the salts of the former differ from those which the latter forms with the same bases.

Hence heat modifies the character of telluric acid much in the same way as that of phosphoric acid. At a heat beyond that required to render it anhydrous, telluric acid loses oxygen and is reduced to tellurous acid. (Pog. Annalen. xxviii. 392.)

Its eq. is 88·2; symb. $Te + 3O$, $\dddot{Te}$, or TeO_3.

Chloride.—Rose obtained it by passing a feeble current of chlorine gas over tellurium at a strong heat, when the chloride passes over as a violet vapour, which at first condenses into a black liquid, and when quite cold becomes a solid of the same colour. By the action of water it deposits metallic tellurium, and the bichloride is dissolved.

Its eq. is 99·62; symb. $Te + Cl$, or $TeCl$.

Bichloride.—Rose obtained this in the same manner as the preceding chloride, except using a lower heat and a more liberal supply of chlorine. The bichloride is also volatile, and after being purified from free chlorine by agitation with mercury, and a second distillation, it condenses into a white crystalline solid. By a gentle heat it yields a brown liquid, but recovers its whiteness on cooling. (Pog. Annalen, xxi. 443.)

Its eq. is 135·04; symb. $Te + 2Cl$, or $TeCl_2$.

Bisulphuret.—This compound falls of a dark brown, nearly black colour, when hydrosulphuric acid gas is transmitted through a solution of bichloride of tellurium, tellurous acid, or any soluble tellurite. This sulphuret is what Berzelius calls a sulphur-acid, forming a soluble sulphur-salt by uniting with sulphuret of potassium. Hence a solution of caustic potassa dissolves bisulphuret of tellurium, producing the same kind of change as on sulphuret of antimony.

Its eq. is 96·4; symb. $Te + 2S$, or TeS_2.

Persulphuret.—This compound falls of a deep yellow colour, when a salt of telluric acid is mixed in solution with persulphuret of potassium. Its existence is but transient, as it is quickly transformed into bisulphuret and becomes black.

Hydrotelluric Acid.—This gas, discovered by Davy in 1809, is formed by acting with hydrochloric acid on an alloy of tellurium with zinc or tin. It has the properties of a feeble acid, very analogous in odour, and apparently in composition, to hydrosulphuric acid; it is absorbed by water, forming a claret-coloured solution; and it precipitates many metallic salts, yielding an alloy of tellurium with the other metal. It is deprived of its hydrogen by chlorine, nitric acid, or oxygen of the atmosphere, tellurium being separated.

Its eq. is 65·2; symb. Te + H, or TeH.

SECTION XXI.

COPPER.

Hist. and Prep.—ONE of the most abundant of the metals, and was well known to the ancients. Native copper is by no means uncommon, being found more or less in most copper mines: it occurs in large amorphous masses in some parts of America, and is sometimes met with in octohedral crystals, or in some of the forms allied to the octohedron. Stromeyer has lately discovered it in several specimens of meteoric iron, but in a quantity not exceeding 2-1000ths of the mass. The copper of commerce is extracted chiefly from the native sulphuret; especially from copper pyrites, a double sulphuret of iron and copper. The first part of the process consists in roasting the ore, so as to burn off some of the sulphur, and leave the remainder as a subsulphate of the oxides of iron and copper. The mass is next heated with some unroasted ore and siliceous substances, by which means much of the iron unites in the state of black oxide with silicic acid, and rises as a fusible slag to the surface; while most of the copper returns to the state of sulphuret. It is then subjected to long-continued roasting, when the greater part of the sulphur escapes as sulphurous acid, and the metal is oxidized; after which it is reduced by charcoal, and more of the iron separated as a silicate by the addition of sand. Lastly, the metal is strongly heated while a current of air plays upon its surface: the impurities, chiefly sulphur and iron, being more oxidable than copper, combine with oxygen by preference, and the copper is at length left in a state of purity sufficient for the purposes of commerce.

Prop.—Distinguished from all other metals, titanium excepted, by having a red colour. It receives a considerable lustre by polishing. Its density, when fused, is 8·667, and it is increased by hammering. It is both ductile and malleable, and in tenacity is inferior only to iron. It is hard and elastic, and consequently sonorous. Its point of fusion is 1996° F. according to Daniell, being less fusible than silver and more so than gold.

It undergoes little change in a perfectly dry atmosphere, but is rusted in a short time by exposure to air and moisture, being converted into a green substance, carbonate of the black oxide of copper. At a red heat it absorbs oxygen, and is converted into black scales of oxide. It is attacked with difficulty by hydrochloric and sulphuric acids, and not at all by solutions of the vegetable acids, if atmospheric air be excluded; but if air have free access, the metal absorbs oxygen with rapidity, the attraction of the acid for the oxide of copper co-operating with that of the copper for oxygen. Nitric acid acts with violence on copper, forming a nitrate of the black oxide.

The most trustworthy experiments for determining the eq. of copper are those of Berzelius on the reduction of the black oxide by means of hydrogen gas at a red heat. According to the best of his analyses, 8 parts of oxygen unite with 31·6 parts of copper to constitute the black oxide; and, therefore, if this oxide be formed of an atom of oxygen united with an atom of copper, the eq. of this metal will be 31·6. This opinion, which I have adopted, is maintained by Thomson, Berzelius, and many Continental chemists. Others consider it as a binoxide, regarding red oxide of copper as the real protoxide; and these take twice 31·6 or 63·2 as an eq. of copper. The principal arguments in favour of the former view are these:—1, the red oxide has very much the character of a *suboxide*, a term frequently used to designate an oxide which has little or no tendency to unite with acids, and which contains less than one atom of oxygen to one atom of metal; 2, the product of the eq. and specific heat of most metals is a constant quantity, and copper coincides with the law, provided the black oxide contain an atom of each element; 3, the salts of the black oxide are isomorphous with the salts of protoxide of iron, which gives a strong presumption that these oxides possess the same atomic constitution.

Its symb. is Cu.

The composition of the compounds described in this section is as follows:—

	Copper.			Equiv.	Formulæ.
Red or Dioxide	63·2	2 eq.+Oxygen	8	1 eq.= 71·2	$2Cu+O$.
Black or Protoxide	31·6	1 eq.+do.	8	1 eq.= 39·6	$Cu+O$.
Superoxide	31·6	1 eq.+do.	16	2 eq.= 47·6	$Cu+2O$.
Dichloride	63·2	2 eq.+Chlorine	35·42	1 eq.= 98·62	$2Cu+Cl$.
Chloride	31·6	1 eq.+do.	35·42	1 eq.= 66·02	$Cu+Cl$.
Diniodide	63·2	2 eq.+Iodine	126·3	1 eq.=189·5	$2Cu+I$.
Disulphuret	63·2	2 eq.+Sulphur	16·1	1 eq.= 79·3	$2Cu+S$.

	Copper.			Equiv.	Formulæ.
Sulphuret . .	31·6	1 eq.+Sulphur	16·1	1 eq.= 47·7	$Cu+S$.
Triphosphuret .	94·8	3 eq.+Phosphorus	15·7	1 eq.=110·5	$3Cu+P$.
Subsesquiphosph.	94·8	3 eq.+do.	31·4	2 eq.=126·2	$3Cu+2P$.

Red Oxide.—Hist. and Prep.—This compound occurs native in the form of octohedral crystals, and is found of peculiar beauty in the mines of Cornwall. It may be prepared artificially by heating in a covered crucible a mixture of 31·6 parts of copper filings with 39·6 of the black oxide; or still better by arranging thin copper plates one above the other with interposed strata of the black oxide, and exposing them to a red heat carefully protected from the air. Another method is by boiling a solution of acetate of protoxide of copper with sugar, when the suboxide subsides as a red powder; and another is to fuse at a low red heat the dichloride of copper with about an equal weight of carbonate or bicarbonate of soda, subsequently dissolving the sea-salt by water, and drying the red powder.

In this case, by an interchange of elements,

1 eq. Dichloride of Copper	Cu_2Cl	yield	1 eq. Red Oxide	Cu_2O
and 1 eq. Soda	NaO		and 1 eq. Chloride of Sodium	$NaCl$.

Malaguti recommends the following process:—100 parts of sulphate of copper and 57 of carbonate of soda, both in crystals, are fused at a gentle heat; and the mass left when all water is expelled, is pulverized and mixed with 25 parts of copper filings. The mixture is pressed into a crucible and exposed for 20 minutes to a white heat. The result is again pulverized and carefully washed (An. de Ch. et Ph. liv. 216).

Prop.—The red oxide of copper has a sp. gr. of 6·093, and in colour is very similar to copper. It may be preserved in a dry atmosphere; but at a red heat it absorbs oxygen and is converted into the protoxide. Dilute acids act on it very slowly; and the resulting solution, as is indicated by its tint, does not arise from the union of the red oxide itself with the acid, but from its being resolved, like other sub-oxides, into metal and a protoxide. With strong nitric acid it is oxidized, binoxide of nitrogen escapes, and a nitrate of the black oxide is formed. Strong hydrochloric acid forms with it a colourless solution, from which alkalies throw it down as a hydrate of an orange tint. In this state it readily absorbs oxygen from the air. The red oxide of copper is soluble in ammonia, and the solution is quite colourless; but it becomes blue with surprising rapidity by free exposure to air, owing to the formation of the black oxide.

Its eq. is 71·2; symb. $2Cu + O$, or Cu_2O.

Black Oxide.—Hist. and Prep.—This compound, the *copper black* of mineralogists, is sometimes found native, being formed by the spontaneous oxidation of other ores of copper. It may be prepared artificially by calcining metallic copper, by precipitation from the salts of copper by means of pure potassa, and by heating nitrate of copper to redness.

Prop.—It varies in colour from a dark brown to a bluish-black, according to the mode of formation; its sp. gr. is 6·401. It undergoes no change by heat alone, but is readily reduced to the metallic state by heat and combustible matter; and is hence much employed as an oxidizing agent in the analysis of organic substances. It is insoluble in water, and does not affect the vegetable blue colours; it combines with nearly all the acids, forming salts which have a green or blue tint. It is soluble likewise in ammonia, forming with it a deep blue solution, a property by which protoxide of copper is distinguished from all other substances. Its salts are distinguished from most substances by their colour, and are easily recognised by reagents. When pure soda or potassa is mixed with a solution of sulphate of the protoxide, a greenish-blue disulphate at first subsides; but as soon as the alkali is added in excess, a blue bulky hydrate of the oxide is formed, which is decomposed by boiling, and consequently becomes black. Pure ammonia also throws down the disulphate when carefully added; but an excess of the alkali instantly redissolves the precipitate, and forms a deep blue solution. Alkaline carbonates cause a bluish-green precipitate, carbonate of the protoxide, which is redissolved by an excess of carbonate of ammonia. It is precipitated as a dark brown sulphuret by hydrosulphuric acid, and as a reddish-brown ferrocyanuret by ferrocyanuret of potassium. It is thrown down of a yellowish-white colour by albumen, and M. Orfila has proved that this compound is inert, so that albumen is an antidote to poisoning by copper.

Copper is separated in the metallic state by a rod of iron or zinc. The copper thus obtained, after being digested in a dilute solution of hydrochloric acid, is almost chemically pure.

The best mode of detecting copper, when supposed to be present in mixed fluids, is by hydrosulphuric acid. The sulphuret, after being collected, and heated to redness in order to char organic matter, should be placed on a piece of porcelain, and be digested in a few drops of nitric acid. Sulphate of protoxide of copper is formed, which, when evaporated to dryness, strikes the characteristic deep blue tint on the addition of ammonia; but the most delicate test of black oxide of copper in solution is ferrocyanide of potassium.

Its eq. is 39·6; symb. $Cu + O$, $\dot{Cu}$, or CuO.

Superoxide.—This oxide was prepared by Thenard by the action of peroxide of hydrogen diluted with water on the hydrated black oxide. It suffers spontaneous decomposition under water; but it may be dried *in vacuo* by means of sulphuric acid.

Its eq. is 47·6; symb. $Cu + 2O$, $\ddot{Cu}$, or CuO_2.

Dichloride.—*Prep.*—When copper filings are introduced into an atmosphere of chlorine gas, the metal takes fire spontaneously, and both the chlorides are generated. The *dichloride* may be conveniently prepared by heating copper filings with twice their weight of corrosive sublimate. In this way it was originally made by Boyle, who termed it *resin of copper*, from its resemblance to common resin. Proust, who called it *white muriate of copper*, procured it by the action of protochloride of tin on chloride of copper; and also by decomposing the chloride by heat, air being excluded. It is slowly deposited in crystalline grains when the green solution of chloride of copper is kept in a corked bottle in contact with metallic copper.

Prop.—The dichloride of copper is fusible at a heat just below redness, and bears a red heat in close vessels without subliming. It is insoluble in water, but dissolves in hydrochloric acid, and is precipitated unchanged by water as a white powder. Its colour varies with the mode of preparation, being white, yellow, or dark brown. It is apt to absorb oxygen from the atmosphere, forming a green-coloured compound of oxide and chloride of copper; a change to which the dichloride prepared in the moist way is peculiarly prone.

Its eq. is 98·62; symb. $2Cu + Cl$, or Cu_2Cl.

Chloride.—The chloride of copper is obtained in solution of a green colour by dissolving protoxide of copper in hydrochloric acid, and crystallizes by due concentration in green needles which are deliquescent and very soluble in alcohol. When heated they fuse, lose water, and the anhydrous chloride in form of a yellow powder is left; but the heat must not exceed 400°, as beyond that degree the chloride loses half its chlorine, and is converted into the dichloride. Its eq. is 66·02; symb. $Cu + Cl$, or $CuCl$.

Diniodide of Copper.—This substance is obtained by adding iodide of potassium to a solution made of the sulphates of the protoxides of copper and iron, both in crystals, in the ratio of 1 to $2\frac{1}{4}$, when the protoxide of iron takes the oxygen of the oxide of copper and the iodine the metallic copper, forming a white precipitate, the diniodide. It may be dried, and will bear a high temperature in close vessels, without change; but if heated with the oxides of iron, manganese, or copper, iodine is expelled and the copper oxidized.

Its eq. is 189·5; symb. $2Cu + I$, or Cu_2I.

Iodide of Copper is scarcely known. For on mixing a salt of oxide of copper with iodide of potassium, iodine is set free and the diniodide of copper falls. A small quantity of iodide of copper remains in solution.

Sulphurets of Copper.—The disulphuret is a natural production, well known to mineralogists under the name of *copper glance;* and in combination with protosulphuret of iron, it is a constituent of variegated copper ore. It is formed artificially by heating copper filings with a third of their weight of sulphur, the combination being attended with such free disengagement of heat, that the mass becomes vividly luminous.

Its eq. is 79·3; symb. $2Cu + S$, or Cu_2S.

Sulphuret of Copper is formed by the action of hydrosulphuric acid on a salt of copper. When ignited without exposure to the air, it loses half of its sulphur, and is converted into the disulphuret.

Its eq. is 47·7; symb. $Cu + S$, or CuS.

Phosphurets of Copper.—Rose states that the triphosphuret is generated by the action of phosphuretted hydrogen gas on dichloride of copper, the mutual interchange of elements being such that

3 eq. Dichloride of Copper	$3Cu_2Cl$	yield	2 eq. Triphosphuret	$2Cu_3P$
and 1 eq. Phosphuretted Hyd.	P_2H_3		and 3 eq. Hydrochl. Acid	$3HCl$.

The subsesquiphosphuret is formed by a similar interchange between chloride of copper and phosphuretted hydrogen, so that

3 eq. Chloride of Copper	$3CuCl$.	yield	1 eq. Subsesquiphosphuret	Cu_3P_2
and 1 eq. Phosp. Hyd.	P_2H_3		and 3 eq. Hydrochloric Acid	$3HCl$.

Rose obtained the protophosphuret by the action of hydrogen gas on phosphate of protoxide of copper at a red heat. All these phosphurets resemble each other, being pulverulent, of a grey colour, insoluble in hydrochloric acid, oxidized and dissolved by nitric acid, and burn with a phosphorous flame before the blowpipe. A phosphuret of copper is also obtained by transmitting phosphuretted hydrogen gas through a solution of sulphate of oxide of copper; but the dark precipitate which falls seems to be a variable mixture of different phosphurets, phosphoric acid being generated at the same time. (An. de Ch. et Ph. li. 47.)

SECTION XXII.

LEAD.

Hist. and Prep.—THIS metal was well known to the ancients. As a native production it is very rare; but in combination with sulphur it occurs in great quantity. All the lead of commerce is extracted from the native sulphuret, the *galena* of mineralogists. This ore, in the state of a coarse powder, is heated in a reverberatory furnace; when part of it is oxidized, yielding sulphate of protoxide of lead, sulphuric acid, which is evolved, and free oxide of lead. These oxidized portions then react on sulphuret of lead: by the reaction of two eq. of oxide of lead and one of the sulphuret, three eq. of metallic lead and one of sulphurous acid result; while one equivalent of the sulphuret and one of sulphate mutually decompose each other, giving rise to two eq. of sulphurous acid and two of metallic lead. The slag which collects on the surface of the fused lead contains a large quantity of sulphate of protoxide of lead, and is decomposed by the addition of quicklime, the oxide so separated reacting as before on sulphuret of lead. The lead of commerce commonly contains silver, iron, and copper.

Prop.—It has a bluish-grey colour, and when recently cut, a strong metallic lustre; but soon tarnishes by exposure to the air, acquiring a superficial coating of carbonate of protoxide of lead. (Christison.) Its sp. gr. is 11·381. It is soft, flexible, and inelastic. It is both malleable and ductile, possessing the former property in particular to a considerable extent. In tenacity, it is inferior to all ductile metals. It fuses at about 612°, and when slowly cooled forms octohedral crystals. It may be heated to whiteness in close vessels without subliming.

Lead absorbs oxygen quickly at high temperatures. When fused in open vessels, a grey film is formed upon its surface, which is a mixture of metallic lead and protoxide; and when strongly heated, it is dissipated in fumes of the protoxide. In distilled water, previously boiled and preserved in close vessels, it undergoes no change; but in open vessels it is oxidized with considerable rapidity, yielding minute, shining, brilliantly white, crystalline scales of carbonate of the protoxide, the oxygen and carbonic acid being derived from the air. The presence of saline matter in water retards the oxidation of the lead; and some salts, even in very minute quantity, prevent it altogether. The protecting influence, exerted by certain substances, was first noticed by Guyton Morveau; but it has been minutely investigated by Christison of Edinburgh, who has discussed the subject in his excellent Treatise on Poisons. He finds that the preservative power of neutral salts is materially connected with the insolubility of the compound which their acid is capable of forming with lead. Thus, phosphates and sulphates, as well as chlorides and iodides, are highly preservative; so small a quantity as 1-30,000th part of phosphate of soda or iodide of potassium in distilled water preventing the corrosion of lead. In a preservative solution the metal gains weight during some weeks, in consequence of its surface gradually acquiring a superficial coating of carbonate, which is slowly decomposed by the saline matter of the solution. The metallic surface being thus covered with an insoluble film, which adheres tenaciously, all further change ceases. Many kinds of spring water, owing to the salts which they contain, do not corrode lead; and hence, though intended for drinking, it may be safely collected in leaden cisterns. Of this, the water of Edinburgh is a remarkable instance.

Lead is not attacked by the hydrochloric or the vegetable acids, though their presence, at least in some instances, accelerates the absorption of oxygen from the atmosphere in the same manner as with copper. Cold sulphuric acid does not act upon it; but when boiled in that liquid, the lead is slowly oxidized at the expense of the acid. The only proper solvent for lead is nitric acid. This reagent oxidizes it rapidly, and forms with its oxide a salt which crystallizes in opaque octohedrons by evaporation.

From my experiments on the composition of the protoxide of lead, and of the nitrate and sulphate of that oxide, I have deduced 103·6 as the eq. a number which agrees very closely with the researches of Berzelius on the same subject. (Phil. Trans. 1833, part ii.) Its symb. is Pb. The composition of its compounds described in this section is as follows :—

	Lead.			Equiv.	Formulæ.
Dinoxide .	207·2	2 eq.+Oxygen .	8	1 eq.=215·2	$2Pb+O$ or Pb_2O.
Protoxide .	103·6	1 eq.+ . . .	8	1 eq.=111·6	$Pb+O$ or PbO.
Sesquioxide	207·2	2 eq.+ . . .	24	3 eq.=231·2	$2Pb+3O$ or Pb_2O_3.

	Lead.			Equiv.	Formulæ.
Peroxide .	103·6	1 eq.+Oxygen .	16	2 eq.=119·6	$Pb+2O$ or PbO_2.
Red Oxide	310·8	3 eq.+ . . .	32	4 eq. } =342·8	$3Pb+4O$.
	or Protox. 223·2	or 2 eq.+Perox.	119·6	1 eq.	$2PbO+PbO_2$.
Chloride .	103·6	1 eq.+Chlorine	35·42	1 eq.=139·02	$Pb+Cl$.
Iodide .	103·6	1 eq.+Iodine .	126·3	1 eq.=229·9	$Pb+I$.
Bromide .	103·6	1 eq.+Bromine .	78·4	1 eq.=182	$Pb+Br$.
Fluoride .	103·6	1 eq.+Fluorine .	18·68	1 eq.=122·28	$Pb+F$.
Sulphuret .	103·6	1 eq.+Sulphur .	16·1	1 eq.=119·7	$Pb+S$.
Phosphuret Carburet	Composition uncertain.				

Dinoxide of Lead.—Dulong observed that on heating dry oxalate of protoxide of lead in a glass tube to low redness, air being excluded, a mixture of carbonic acid and carbonic oxide gases is evolved, and a suboxide remains of a dark grey, nearly black, colour. Boussingault has lately proved that it is a dinoxide. It does not unite with acids, but is resolved by them into a salt of the protoxide with separation of metallic lead. (An. de Ch. et Ph. liv. 263.) Its eq. is 215·2; symb. $2Pb+O$, or Pb_2O.

Protoxide.—*Prep.*—This oxide is prepared on a large scale by collecting the grey film which forms on the surface of melted lead, and exposing it to heat and air until it acquires a uniform yellow colour. In this state it is the *massicot* of commerce; and when partially fused by heat, the term *litharge* is applied to it. As thus procured it is always mixed with the red oxide. It may be obtained pure by adding ammonia to a cold solution of nitrate of protoxide of lead until it is faintly alkaline, washing the precipitated subnitrate with cold water, and when dry, heating it to moderate redness for an hour in a platinum crucible. An open fire should be used, and great care taken to prevent combustible matter in any form from contact with the oxide.

Prop.—It is red while hot, but has a rich lemon-yellow colour when cold, is insoluble in water, fuses at a bright red heat, and is fixed and unchangeable in the fire. Its sp. gr. is 9·4214. The fused protoxide has a highly foliated texture, and is very tough, so as to be pulverized with difficulty. By transmitted light it is yellow; but by reflected light it appears green in some parts and yellow in others. Heated with combustible matters it parts with oxygen, and is reduced. From its insolubility it does not change the vegetable colours under common circumstances; but when rendered soluble by a small quantity of acetic acid, it has a distinct alkaline reaction. It unites with acids, and is the base of all the salts of lead, most of which are of a white colour. From its solutions it is precipitated by pure alkalies as a white hydrate, which is redissolved by potassa in excess; as a white carbonate, which is the well-known pigment *white lead*, by alkaline carbonates; as a white sulphate by soluble sulphates; as a dark brown sulphuret by hydrosulphuric acid; and as yellow iodide of lead by hydriodic acid or iodide of potassium.

With regard to the poisonous property of the salts of lead, a remarkable fact has been observed by my colleague Dr. A. T. Thomson, who has proved that of all the ordinary preparations of lead, the carbonate is by far the most virulent poison. Any salt of lead which is easily convertible into the carbonate, as for instance the subacetate, is also poisonous; but he has given large doses of the nitrate of the protoxide and chloride of lead to rabbits without producing perceptible inconvenience. He finds that acetate of protoxide of lead, mixed with vinegar to prevent the formation of any carbonate, may be freely and safely administered in medical practice.

The best method of detecting the presence of lead in wine or other suspected mixed fluids is by means of hydrosulphuric acid. The sulphuret of lead, after being collected on a filter and washed, is to be digested in nitric acid diluted with twice its weight of water, until the dark colour of the sulphuret disappears. The solution of the nitrate should then be brought to perfect dryness on a watch-glass, in order to expel the excess of nitric acid, and the residue be redissolved in a small quantity of cold water. On dropping a particle of iodide of potassium into a portion of this liquid, yellow iodide of lead will instantly appear.

Protoxide of lead unites readily with earthy substances, forming with them a transparent colourless glass. Owing to this property it is much employed for glazing earthenware and porcelain. It enters in large quantity into the composition of flint glass, which it renders more fusible, transparent, and uniform.

Lead is separated from its salts in the metallic state by iron or zinc. The best way of demonstrating this fact is by dissolving one part of acetate of protoxide of lead in 24 of water, and suspending a piece of zinc in the solution by means of a thread. The lead is deposited upon the zinc in a peculiar arborescent form, giving rise to the appearance called *arbor saturni*.

Its eq. is 111·6; symb. $Pb + O$, $\dot{Pb}$, or PbO.

Red Oxide.—*Prep.*—This compound, the *minium* of commerce, is employed as a pigment, and in the manufacture of flint glass.

It is formed by oxidizing lead by heat and air without allowing it to fuse, and then exposing it in open vessels to a temperature of 600° or 700°, while a current of air plays upon its surface. It slowly absorbs oxygen and is converted into minium.

Prop.—This oxide does not unite with acids. When heated to redness it gives off pure oxygen gas, and is reconverted into the protoxide. When digested in nitric acid it is resolved into protoxide and peroxide of lead, the former of which unites with the acid, while the latter remains as an insoluble powder. From the facility with which this change is effected even by acetic acid, most chemists consider red lead, not so much as a definite compound of lead and oxygen, but as a salt composed of the protoxide and peroxide, as stated at page 521. This oxide has been long considered as a sesquioxide, an error first corrected by Dalton (New System of Chemistry, ii. 41), whose observation has been confirmed by Dumas and Phillips. (An. de Ch. et Ph. xlix. 398, and Phil. Mag. N.S. iii. 125.) Dumas shows that the minium is not uniform in composition, but consists of variable mixtures of the protoxide with real red lead. The former may be oxidized by continued exposure to air and heat, and may be dissolved by acetic acid very much diluted with cold water.

Its eq. is 342·8 ; symb. $2PbO + PbO_2$.

Sesquioxide.—Winkelblech (Ann. der Pharm. xxi. 29) has proved the existence of this compound. It is prepared by adding hypochlorite of soda to a solution of protoxide of lead in caustic potash. It forms a reddish-yellow insoluble powder, which is resolved by heat and by acids into protoxide and oxygen. Its eq. is 231·2 ; symb. Pb_2O_3. Red lead may be a compound of 1 at. sesquioxide and 1 at. protoxide, Pb_2O_3, $PbO = Pb_3O_4$.

Peroxide.—*Prep.*—This oxide may be obtained by the action of nitric acid on minium, as just mentioned; by fusing protoxide of lead with chlorate of potassa, at a temperature short of redness, and removing the chloride of potassium by solution in water; and by transmitting a current of chlorine gas through a solution of acetate of the protoxide of lead. In the last the reaction is such, that

1 eq. Chlorine and	2 eq. Protox. Lead	yield	1 eq. Perox. Lead and	1 eq. Chloride Lead
Cl	$2PbO$		PbO_2	$PbCl$.

The chloride is removed by washing with warm water.

Prop.—It is of a puce colour, is insoluble in water, and is resolved by strong ox-acids, such as the sulphuric and nitric, into a salt of the protoxide and oxygen gas. With hydrochloric acid it yields chlorine gas and chloride of lead. At a red heat it emits oxygen gas and is converted into the protoxide.

Its eq. is 119·6; symb. $Pb + 2O$, $\ddot{Pb}$, or PbO_2.

Chloride of Lead.—This compound, sometimes called *horn lead*, is slowly formed by the action of chlorine gas on thin plates of lead, and may be obtained more easily by adding hydrochloric acid or a solution of sea-salt to acetate or nitrate of oxide of lead dissolved in water. This chloride dissolves to a considerable extent in hot water, especially when acidulated with hydrochloric acid, and separates on cooling in small acicular anhydrous crystals of a white colour. It fuses at a temperature below redness, and forms as it cools a semi-transparent mass, which has a density of 5·133. It bears a full red heat in close vessels without subliming; but in open vessels it smokes from spurious evaporation, loses some of its chlorine and absorbs oxygen, yielding an oxychloride of a yellow colour. Its eq. is 139·02; symb. $Pb + Cl$, or $PbCl$.

Iodide of Lead is easily formed by mixing a solution of hydriodic acid in excess with the nitrate of protoxide of lead dissolved in water; and it is of a rich yellow colour. It is dissolved by boiling water, forming a colourless solution, and is deposited on cooling in yellow crystalline scales of a brilliant lustre.

Its eq. is 229·9; symb. $Pb + I$, or PbI.

Bromide of Lead.—It falls as a white crystalline powder, of sparing solubility in water, when a soluble salt of lead is mixed with bromide of potassium in solution. Exposed to heat it fuses into a red liquid which becomes yellow when cold.

Its eq. is 182; symb. $Pb + Br$, or $PbBr$.

Fluoride of Lead is formed by mixing hydrofluoric acid with acetate of protoxide of lead, and falls as an uncrystalline white powder of very sparing solubility. It is soluble in nitric and hydrochloric acids, but is decomposed when the solution is evaporated.

Its eq. is 122·28; symb. $Pb + F$, or PbF.

Sulphurets of Lead.—It is probable that lead unites with sulphur in several different proportions; but the only one of these compounds well known to chemists is the native sulphuret, *galena*, which occurs in cubic crystals, or in forms allied to the cube. It may be formed artificially by fusing lead with sulphur, or by the action of hydrosulphuric acid on a salt of lead.

Its eq. is 119·7; symb. $Pb + S$, or PbS.

Phosphuret of Lead has been little examined. It may be formed by heating phosphate of oxide of lead with charcoal, by mixing a solution of phosphorus in alcohol or ether with the solution of a salt of lead, or by the action of phosphuretted hydrogen on a similar solution.

Carburet of Lead may be obtained by reducing oxide of lead in a state of fine division and intimate admixture with charcoal. It is also generated when salts of lead, which contain a vegetable acid, are decomposed by heat in close vessels. (Berzelius.)

CLASS II.

ORDER III.

METALS, THE OXIDES OF WHICH ARE REDUCED TO THE METALLIC STATE BY RED HEAT.

SECTION XXIII.

MERCURY OR QUICKSILVER.

Hist. and Prep.—This metal was well known to the ancients. The principal mines from which it is obtained are those of Idria in Carniola and Almaden in Spain, where it is found both in the native state and combined with sulphur as cinnabar, the latter being the most abundant. From this ore the metal is extracted by heating it with lime or iron filings, by which means the mercury is volatilized and the sulphur retained. As prepared on a large scale it is usually mixed in small quantity with other metals, from which it may be purified by cautious distillation.

Prop.—Distinguished from all other metals by being fluid at common temperatures. It has a tin-white colour and strong metallic lustre. It becomes solid at a temperature which is 39 or 40 degrees below zero; and in congealing, it evinces a strong tendency to crystallize in octohedrons. It contracts greatly at the moment of congelation; for while its density at 47° is 13·545, that of frozen mercury is 15·612. When solid it is malleable, and may be cut with a knife. At 62° or near that degree, it enters into ebullition, and condenses again on cool surfaces into metallic globules.

Mercury, if quite pure, is not tarnished in the cold by exposure to air and moisture; but if it contain other metals, the amalgam of those metals oxidizes readily, and collects as a film upon its surface. It is said to be oxidized by long agitation in a bottle half full of air, and the oxide so formed was called by Boerhaave *Ethiops per se;* but it is very probable that the oxidation of mercury observed under these circumstances was solely owing to the presence of other metals. When exposed to air or oxygen gas, while in the form of vapour, it slowly absorbs oxygen, and is converted into peroxide of mercury.

The only acids that act on mercury are the sulphuric and nitric acids. The former has no action whatever in the cold; but on the application of heat, the mercury is oxidized at the expense of the acid, pure sulphurous acid gas is disengaged, and a sulphate of mercury is generated. Nitric acid acts energetically upon mercury both with and without the aid of heat, oxidizing and dissolving it with evolution of peroxide of nitrogen.

From some late analyses on the peroxide and chlorides of mercury, I have inferred that its equivalent is 202 (Phil. Trans. 1833, part ii.); its symb. is Hg. The composition of its compounds described in this section is as follows:—

	Mercury.			Equiv.	Formulæ.
Protoxide	202	1 eq.+Oxygen	8	1 eq.=210	$Hg+O$ or HgO.
Peroxide	202	1 eq.+do.	16	2 eq.=218	$Hg+2O$ or HgO_2.
Protochloride	202	1 eq.+Chlorine	35·42	1 eq.=237·42	$Hg+Cl$ or $HgCl$.
Bichloride	202	1 eq.+do.	70·84	2 eq.=272·84	$Hg+2Cl$ or $HgCl_2$.
Iodide	202	1 eq.+Iodine	126·3	1 eq.=328·3	$Hg+I$ or HgI.
Sesquiodide	404	2 eq.+do.	378·9	3 eq.=782·9	$2Hg+3I$ or Hg_2I_3.
Biniodide	202	1 eq.+do.	252·6	2 eq.=454·6	$Hg+2I$ or HgI_2.
Protobromide	202	1 eq.+Bromine	78·4	1 eq.=280·4	$Hg+Br$ or $HgBr$.
Bibromide	202	1 eq +do.	156·8	2 eq.=358·8	$Hg+2Br$ or $HgBr_2$.
Protosulphuret	202	1 eq.+Sulphur	16·1	1 eq.=218·1	$Hg+S$ or HgS.
Bisulphuret	202	1 eq.+do.	32·2	2 eq.=234·2	$Hg+2S$ or HgS_2.
Ioduretted bichloride of Mercury . .		$HgCl_2$ I	5456·8 126·3	20 eq. 1 eq.	=5583·1 $20HgCl_2+I$.
Iodo-bichloride of Mercury . . .		$HgCl_2$ HgI_2	10913·6 454·6	40 eq. 1 eq.	=11368·2 $40HgCl_2+HgI_2$.

Protoxide.—Prep.—Best by the process recommended by Donovan (An. of Phil. xiv.): this consists in mixing calomel briskly in a mortar with pure potassa in excess, so as to effect its decomposition as rapidly as possible; the protoxide is then washed with cold water, and dried spontaneously in a dark place. These precautions are rendered necessary by the tendency of the protoxide to resolve itself into the peroxide and metallic mercury, a change which is easily effected by heat, by the direct solar rays, and even by daylight. It is on this account very difficult to procure protoxide of mercury in a state of absolute purity.

Prop.—A black powder, which is exceedingly prone to decomposition, is insoluble in water, unites with acids, but is a weak alkaline base. It is precipitated from a solution of its salts, of which the nitrate is the most interesting, as the black protoxide by pure alkalies; as a white carbonate, which soon becomes dark from the loss of carbonic acid, by alkaline carbonates; as calomel by hydrochloric acid or any soluble chloride; and as the black protosulphuret by hydrosulphuric acid. Of these tests, the action of hydrochloric acid is the most characteristic. The oxide is reduced to the metallic state by copper, phosphorous acid, or protochloride of tin.

Its eq. is 210; symb. $Hg + O$, $\dot{Hg}$, or HgO.

Peroxide.—*Prep.*—Either by the combined agency of heat and air, as already mentioned, or by dissolving mercury in nitric acid, and exposing the nitrate so formed to a temperature just sufficient for expelling the whole of the nitric acid. It is commonly known by the name of *red precipitate.* The peroxide prepared from the nitrate almost always contains a trace of nitric acid, which may be detected by heating it in a clean glass tube by means of a spirit-lamp: a yellow ring, formed of subnitrate of oxide of mercury, collects within the tube just above the part which is heated. (Clark.)

As thus prepared, it is commonly in the form of shining crystalline scales of a nearly black colour while hot, but red when cold: when very finely levigated, the peroxide has an orange colour. It is soluble to a small extent in water, forming a solution which has an acrid metallic taste, and communicates a green colour to the blue infusion of violets. When heated to redness, it is converted into metallic mercury and oxygen. Long exposure to light has a similar effect. (Guibourt.)

Some of the neutral salts of this oxide, such as the nitrate and sulphate, are converted by water, especially at a boiling temperature, into insoluble yellow subsalts, leaving a strongly acid solution, in which a little of the original salt is dissolved. This oxide is separated from all acids as a yellow hydrate, by the pure fixed alkalies. Carbonate of potash or soda causes a dirty brownish red precipitate. Ammonia and its carbonate cause a white precipitate, which is a double salt, consisting of one equivalent of the acid, one equivalent of the peroxide, and one equivalent of ammonia. The oxide is readily reduced to the metallic state by metallic copper. Hydrosulphuric acid, phosphorous acid, and protochloride of tin, reduce the peroxide into the protoxide; and when added in larger quantity, the first throws down a black sulphuret, and the two latter metallic mercury. The action of hydrosulphuric acid on a solution of corrosive sublimate is, however, peculiar; for at first it occasions a white precipitate which, according to Rose, is a compound of two equivalents of bisulphuret to one of bichloride of mercury. This gas acts on bibromide and biniodide of mercury in a similar manner. (An. de Ch. et Ph. xl. 46.)

Its eq. is 218; symb. $Hg + 2O$, $\ddot{Hg}$, or HgO_2.

Protochloride.—Prep.—Protochloride of mercury, or *calomel*, is a rare mineral production, called horn silver, which occurs crystallized in quadrangular prisms terminated by pyramids. It is always generated when chlorine comes in contact with mercury at common temperatures; and also by the contact of metallic mercury and the bichloride. It may be made by precipitation, by mixing nitrate of protoxide of mercury in solution with hydrochloric acid or any soluble chloride. It is more commonly prepared by sublimation. This is conveniently done by mixing 272·84 parts or 1 eq. of the bichloride with 202 parts or 1 eq. of mercury, until the metallic globules entirely disappear, and then subliming. When first prepared it is always mixed with some corrosive sublimate, and therefore should be reduced to powder and well washed before being employed for chemical or medical purposes.

Prop.—When obtained by sublimation it is in semi-transparent crystalline cakes; but as formed by precipitation, it is a white powder. Its sp. gr. is 7·2. At a heat short of redness, but higher than the subliming point of the bichloride, it rises in vapour without previous fusion; but during the sublimation a portion is always resolved into mercury and the bichloride. It is yellow while warm, but recovers its whiteness on cooling. It is distinguished from the bichloride by not being poisonous, by having no taste, and by being exceedingly insoluble in water. Acids have little effect upon it; but pure alkalies decompose it, separating the black protoxide of mercury. When calomel is boiled in a solution of hydrochlorate of ammonia, it is converted into corrosive sublimate and metallic mercury. Chloride of sodium has a similar effect, though in a less degree. It eq. is 237·42; symb. $Hg + Cl$, or $HgCl$.

Bichloride.—Prep.—When mercury is heated in chlorine gas, it takes fire, and burns with a pale red flame, forming the well-known medicinal preparation and virulent poison *corrosive sublimate* or bichloride of mercury. It is prepared for medical purposes by subliming a mixture of bisulphate of the peroxide of mercury with chloride of sodium or sea-salt. The exact quantities required for mutual decomposition are 298·2 parts or 1 eq. of the bisulphate, to 117·44 parts or 2 eq. of the chloride. Thus,

Bisulphate of Mercury		1 eq.
Sulphuric Acid .	80·2 or 2 eq.	$2SO_3$.
Peroxide of Mer. .	218 or 1 eq.	HgO_2.
	298·2	HgO_2+2SO_3.

Chloride of Sodium		2 eq.
Chlorine .	70·84 or 2 eq.	2 Cl.
Sodium .	46·6 or 2 eq.	2 Na.
	117·44	2 NaCl.

And by mutual interchange of elements they produce

Bichloride of Mercury		1 eq.
Mercury .	202 or 1 eq.	. Hg.
Chlorine .	70·84 or 2 eq.	. 2Cl.
	272·84	$HgCl_2$.

Sulphate of Soda		2 eq.
Soda . . .	62·6 or 2 eq.	. 2NaO.
Sulphuric Ac.	80·2 or 2 eq.	. $2SO_3$.
	142·8	$2NaO,SO_3$.

The products have exactly the same weight (272·84 + 142·8 = 415·64) as the compounds (298·2 + 117·44 = 415·64) from which they were prepared.

Prop. — When obtained by sublimation, it is a semi-transparent colourless substance, of a crystalline texture. It has an acrid, burning taste, and leaves a nauseous metallic flavour on the tongue. Its sp. gr. is 5·2. When exposed to a heat short of incandescence, it is fused, enters into ebullition from the rapid formation of vapour, and is deposited without further change on cool surfaces as a white crystalline sublimate. It requires twenty times its weight of cold, and only twice its weight of boiling water for solution, and is deposited from the latter, as it cools, in the form of prismatic crystals. Strong alcohol and ether dissolve it in the same proportion as boiling water; and it is soluble in half its weight of concentrated hydrochloric acid at the temperature of 70°. With the chlorides of potassium and sodium, hydrochlorate of ammonia, and several other bases, it enters into combination, forming double salts, which are more soluble than the chloride itself. When its solution in water is agitated with ether, the latter abstracts the bichloride, and rises with it to the surface of the former, thus affording strong evidence of the bichloride having existed as such in the water. Its aqueous solution is gradually decomposed by light, calomel being deposited.

The pure and carbonated fixed alkalies throw down the peroxide of mercury, from a solution of corrosive sublimate. Ammonia, on the contrary, causes the deposition of a white matter, which is commonly known under the name of the white precipitate. This substance has been recently examined by Kane. (Trans. Irish Academy, xvii.) He finds that on adding a slight excess of ammonia just one half of the chlorine of the corrosive sublimate falls, the other half remaining in the solution with ammonia. The precipitate nevertheless does not contain calomel, as is proved by its complete solubility in hydrochloric and nitric acids. From his analysis it is composed of

Mercury . . .	78·6	Ammonia	6·77
Chlorine . . .	13·85	Hygrometric water, loss, & oxygen	0·78

Its atomic constitution would appear from this analysis to contain the compound radical which is the base of the amides. By the action of boiling water, it loses half its chlorine and ammonia, peroxide of mercury being at the same time formed, and a canary-yellow powder is produced. Kane finds that on treating calomel with ammonia, it too loses only one half its chlorine, and a compound analogous to white precipitate is obtained.

The presence of mercury in a fluid supposed to contain corrosive sublimate, may be detected by concentrating and digesting it with an excess of pure potassa. Oxide of mercury, which subsides, is then sublimed in a small glass tube by means of a spirit-lamp, and obtained in the form of metallic globules. But in cases of poisoning, when the bichloride is mixed with organic substances, Christison recommends that the liquid, without previous filtration, be agitated with a fourth of its volume of ether, which separates the poison from the aqueous part, and rises to the surface. The ethereal solution is then evaporated on a watch glass, the residue dissolved in hot water, and the mercury precipitated in the metallic state by protochloride of tin at a boiling temperature. If, as is probable, most of the poison is already converted into calomel, and thereby rendered insoluble, as many vegetable fibres should be picked out as possible, and the whole at once digested with protochloride of tin. The organic substances are then dissolved in a hot solution of caustic potassa, and the insoluble parts washed and sublimed to separate the mercury. (Christison on Poisons.)

A very elegant method of detecting the presence of mercury is to place a drop of the suspected liquid on polished gold, and to touch the moistened surface with a piece of iron wire or the point of a penknife, when the part touched instantly becomes white, owing to the formation of an amalgam of gold. This process was originally suggested by Sylvester, and has since been simplified by Paris. (Medical Jurisprudence, by Paris and Fonblanque.)

Many animal and vegetable solutions convert bichloride of mercury into calomel, a portion of hydrochloric acid being set free at the same time. Some substances effect this change slowly; while others, and especially albumen, produce it in an instant. Thus, when a solution of corrosive sublimate is mixed with albumen, a white flocculent precipitate subsides, which Orfila has shown to be a compound of calomel and albumen, and which he has proved experimentally to be inert. (Toxicologie, vol. i.) Consequently, a solution of the white of eggs is an antidote to poisoning by corrosive sublimate. The muscular and membranous parts, even of a living animal, produce a similar effect; and the causticity of corrosive sublimate seems owing to the destruction of the animal fibre, by which the decomposition of the bichloride is accompanied, and which constitutes an essential part of the chemical change.

Its eq. is 272·84; symb. $Hg + 2Cl$, or $HgCl_2$.

Protiodide of Mercury.—This compound is obtained by mixing nitrate of protoxide of mercury in solution with iodide of potassium. It is a green powder, insoluble in water, and disposed to resolve itself under the influence of heat or solar light into mercury and the biniodide. However, when the heat is quickly supplied, it is fused and sublimed without material change.

Its eq. is 328·3; symb. $Hg + I$, or HgI.

Sesquiodide.—This compound falls as a yellow powder when iodide of potassium is added in solution to the mixed nitrates of the protoxide and peroxide of mercury, the latter being in excess. The precipitate is digested with a solution of sea-salt, which takes up any biniodide which may have fallen.

Its eq. is 782·9; symb. $2Hg + 3I$, or Hg_2I_3.

Biniodide.—This compound is formed by mixing nitrate of the peroxide or bichloride of mercury with iodide of potassium in solution, and falls as a rich red-coloured powder of a tint which vies in beauty with that of vermilion, though, unfortunately, the colour is less permanent. Though insoluble in water, it dissolves freely in an excess of either of its precipitants. If taken up in a hot solution of nitrate of peroxide of mercury, the biniodide crystallizes out on cooling in scales of a beautiful red tint. The same crystals separate from a solution in iodide of potassium; but if the liquid be concentrated, a double iodide of mercury and potassium subsides.

The biniodide, when exposed to a moderate heat, gradually becomes yellow; and the particles, though previously in powder, acquire a crystalline appearance. At about 400° it forms a yellow liquid, which slowly sublimes in small transparent scales, or in large rhombic tables, when a considerable quantity is sublimed. The crystals retain their yellow colour at 60° if kept very tranquil; but if the temperature be below a certain point, or they are rubbed or touched, they quickly become red. This phenomenon is entirely due to a change in molecular arrangement: the different colours so often witnessed in the same substances at different temperatures, as in peroxide of mercury and the protoxides of lead and zinc, appear to be phenomena of the same nature.

Its eq. is 454·6; symb. $Hg + 2I$, or HgI_2.

Ioduretted Bichloride of Mercury.—This compound has recently been described by Lassaigne. (An. de Ch. et Ph. lxiii. 106.) It is formed by adding to an alcoholic solution of iodine a solution of corrosive sublimate, when the deep colour of the iodine gradually disappears, and a colourless solution is obtained. It is remarkable, that in this combination the iodine cannot be detected by starch and chlorine or sulphurous acid, as in its other combinations. The compound is decomposed by heat, but may be obtained in crystals by evaporating a concentrated solution at a moderate temperature. Its eq. is 5583·1; symb. $20HgCl_2 + I$.

Iodo-bichloride of Mercury.—This compound was described by Boullay. (An. de Ch. et Ph. xxxvi. 366.) It is formed by dissolving biniodide of mercury in corrosive sublimate, when a colourless crystalline compound is obtained. It is composed of 40 eq. of the bichloride and one of the biniodide.

Its eq. is 11368·2; symb. $40HgCl_2 + HgI_2$.

Protobromide of Mercury.—It is precipitated as a white insoluble powder by mixing nitrate of protoxide of mercury with bromide of potassium. Its eq. is 280·4; symb. $Hg + Br$, or $HgBr$.

The bibromide is a white crystallizable compound, soluble in water and alcohol, fusible and volatile, and in many respects analogous to the bichloride. It is formed by acting on peroxide of mercury with hydrobromic acid, or digesting the preceding compound with bromine.

Its eq. is 358·8; symb. $Hg + 2Br$, or $HgBr_2$.

Sulphurets of Mercury.—The protosulphuret may be prepared by transmitting a current of hydrosulphuric acid gas through a dilute solution of nitrate of protoxide of mercury, or through water in which calomel is suspended. It is a black-coloured substance, which is oxidized by digestion in strong nitric acid. When exposed to heat it is resolved into the bisulphuret and metallic mercury. Its eq. is 218·1; symb. Hg + S, or HgS.

The bisulphuret is formed by fusing sulphur with about six times its weight of mercury, and subliming in close vessels. When procured by this process it has a red colour, and is known by the name of *factitious cinnabar*. Its tint is greatly improved by being reduced to powder, in which state it forms the beautiful pigment *vermilion*. It may be obtained in the moist way by pouring a solution of corrosive sublimate into an excess of hydrosulphate of ammonia. A black precipitate subsides, which acquires the usual red colour of cinnabar when sublimed. The black precipitate formed by the action of hydrosulphuric acid on bicyanuret of mercury, is likewise a bisulphuret. Cinnabar, as already mentioned, occurs native.

When equal parts of sulphur and mercury are triturated together until metallic globules cease to be visible, the dark-coloured mass called *Ethiops mineral* results, which Mr. Brande has proved to be a mixture of sulphur and bisulphuret of mercury. (Journal of Science, vol. xviii. p. 294.)

Cinnabar is not attacked by alkalies, or any simple acid; but it is dissolved by the nitro-hydrochloric, with formation of sulphuric acid and peroxide of mercury.

Its eq. is 234·2; symb. Hg + 2S, or HgS_2.

SECTION XXIV.

SILVER.

Hist.—THIS metal was known to the ancients. It frequently occurs native in silver mines, both massive and in octohedral or cubic crystals. It is also found in combination with gold, tellurium, antimony, copper, arsenic, and sulphur. In the state of sulphuret it so frequently accompanies galena, that the lead of commerce is rarely quite free from traces of silver.

Prep.—Silver is extracted from its ores by two processes which are essentially distinct; one of them being contrived to separate it from lead, the other, the process by *amalgamation*, being especially adapted to those ores which are free from lead. The principle of its separation from lead is founded on the different oxidability of lead and silver, and on the ready fusibility of litharge. The lead obtained from those kinds of galena which are rich in sulphuret of silver is kept at a red heat in a flat furnace, with a draught of air constantly playing on its surface: the lead is thus rapidly oxidized; and as the oxide, at the moment of its formation, is fused, and runs off through an aperture in the side of the furnace, the production of litharge goes on uninterruptedly until all the lead is removed. The button of silver is again fused in a smaller furnace, resting on a porous earthen dish, made with lixiviated wood-ashes, called a *test*, the porosity of which is so great, that it absorbs any remaining portions of litharge which may be formed on the silver.

Mr. Pattinson of Newcastle has taken out a patent for a new and ingenious process, whereby the extraction of silver from lead is much facilitated. The lead is melted and allowed to cool slowly. The crystals which form first are much richer in silver than the original mass. They are removed by means of a perforated ladle, and the process is repeated both with them and with the residue, till there is obtained, on the one hand, lead almost free of silver, while on the other, the whole silver is collected in combination with a small part of the lead. This mixture is then subjected to cupellation, which from its smaller bulk is more easily and rapidly accomplished.

The ores commonly employed in the process of amalgamation, which has been long used at Freyberg in Saxony, and is extensively practised in the silver and gold mines of South America, are native silver and its sulphuret. At Freyberg the ore in fine powder is mixed with sea-salt, and carefully roasted in a reverberatory furnace. The production of sulphuric acid leads to the formation of sulphate of soda, while the chlorine of the sea-salt combines with silver. The roasted mass is ground to a fine powder, and, together with mercury, water, and fragments of iron, is put into barrels, which are made to revolve by machinery. In this operation, intended to insure perfect contact between the materials, chloride of silver is decomposed by the iron, the silver unites with the mercury, and the chloride of iron is dissolved by the water. The mercury is then squeezed through leathern bags, the pores of which permit the pure mercury to pass, but retain the amalgam of silver. The combined mercury is then distilled off in close vessels, and the metals obtained in a separate state.

Goldsmiths' silver commonly contains copper and traces of gold, the latter appearing in dark flocks when the metal is dissolved in nitric acid. It may be obtained pure for chemical uses by placing a clean piece of copper in a solution of nitrate of oxide of silver, washing the precipitate with pure water, and then digesting it in ammonia, in order to remove any adhering copper. A better process is to decompose chloride of silver by means of carbonate of potassa. For this purpose precipitate a solution of nitrate of oxide of silver with chloride of sodium, wash the precipitate with water, and dry it. Then put twice its weight of carbonate of potassa into a clean hessian or black-lead crucible, heat it to redness, and throw the chloride by successive portions into the fused alkali. Effervescence takes place from the evolution of carbonic acid and oxygen gases, chloride of potassium is generated, and metallic silver subsides to the bottom. The pure metal may be granulated by pouring it while fused from a height of seven or eight feet into a vessel of water.

Prop.—It has the clearest white colour of all the metals, and is susceptible of receiving a lustre surpassed only by polished steel. In malleability and ductility it is inferior only to gold, and its tenacity is considerable. It is very soft when pure, so that it may be cut with a knife. Its density after being hammered is 10·51. At a full red heat, corresponding to 1873° F. according to Daniell, it enters into fusion. It does not rust by exposure to air and moisture. When fused in open vessels it absorbs oxygen in considerable quantity, amounting sometimes to 22 times its volume; but it parts with the whole of it in the act of becoming solid. This fact, first noticed by M. Lucas, has been studied by Gay-Lussac, who attributes to it the peculiarly beautiful aspect of granulated silver: he observed the absorption and subsequent evolution of oxygen to be most abundant in the purest silver, and is entirely prevented by a very small per centage of copper. If silver is heated to redness, without fusing, in contact with glass or porcelain, it readily absorbs oxygen, and the oxide fuses with the earthy matters, forming a yellow enamel. When silver in the form of leaves or fine wire is intensely heated by means of electricity, galvanism, or the oxy-hydrogen blowpipe, it burns with vivid scintillations of a greenish-white colour.

The only pure acids that act on silver are the sulphuric and nitric acids, by both of which it is oxidized, forming with the first a sulphate, and with the second a nitrate of oxide of silver. It is not attacked by sulphuric acid unless by the aid of heat. Nitric acid is its proper solvent, and forms with its oxide a salt, which, after fusion, is known by the name of *lunar caustic*.

From recent experiments on the composition of the chloride and nitrate of the oxide of silver, I have deduced 108 as the eq. of silver, an estimate closely corresponding with the previous researches of Berzelius. (Phil. Trans. 1833, part ii.) Its symb. is Ag. The compounds of silver described in this section are thus constituted:—

	Silver.				Equiv.	Formulæ.
Oxide . .	108	1 eq.+Oxygen	8	1 eq.=116		$Ag+O$ or AgO.
Chloride .	108	1 eq.+Chlorine	35·42	1 eq.=143·42		$Ag+Cl$ or $AgCl$.
Iodide . .	108	1 eq.+Iodine	126·3	1 eq.=234·3		$Ag+I$ or AgI.
Sulphuret .	108	1 eq.+Sulphur	16·1	1 eq.=124·1		$Ag+S$ or AgS.

Oxide of Silver.—This oxide is best procured by mixing a solution of pure baryta with nitrate of oxide of silver dissolved in water. It is of a brown colour, insoluble in water, and is completely reduced by a red heat. It is separated from its solution in nitric acid by pure alkalies and alkaline earths as the brown oxide, which is redissolved by ammonia in excess; by alkaline carbonates as a white carbonate, which is soluble in an excess of carbonate of ammonia; as a dark brown sulphuret by hydrosulphuric acid; and as a white curdy chloride of silver, which is turned violet by light, and is very soluble in ammonia, by hydrochloric acid or any soluble chloride. By the last character, silver may be both distinguished and separated from other metallic bodies.

Silver is precipitated in the metallic state by most other metals. When mercury is employed for this purpose, the silver assumes a beautiful arborescent appearance, called *arbor Dianæ.* A very good proportion for the experiment is 20 grains of lunar caustic to 6 drachms or an ounce of water. The silver thus deposited always contains mercury.

When oxide of silver, recently precipitated by baryta or lime-water, and separated from adhering moisture by bibulous paper, is left in contact for 10 or 12 hours with a strong solution of ammonia, the greater part of it is dissolved; but a black powder remains which detonates violently from heat or percussion. This substance, which was discovered by Berthollet, (An. de Chimie, i.) appears to be a compound of ammonia and oxide of silver; for the products of its detonation are metallic silver, water, and nitrogen gas. It should be made in very small quantity at a time, and dried spontaneously in the air

On exposing a solution of oxide of silver in ammonia to the air, its surface becomes covered with a pellicle, which Faraday considers to be an oxide containing a smaller proportion of oxygen than that just described. This opinion he has made highly probable; but further experiments are requisite before the existence of this oxide can be regarded as certain.

Its eq. is 116; symb. $Ag + O$, $\dot{Ag}$, or AgO.

Chloride of Silver.—Prep.—This compound, which sometimes occurs in silver mines, and constitutes the horn silver of mineralogists, is always generated when silver is heated in chlorine gas, and may be prepared conveniently by mixing hydrochloric acid, or any soluble chloride, with a solution of nitrate of oxide of silver. As formed by precipitation it is quite white; but by exposure to the direct solar rays it becomes violet, and almost black, in the course of a few minutes; and a similar effect is slowly produced by diffused day-light. On this principle is founded Mr. Talbot's method of photography. Hydrochloric acid is set free during this change, and, according to Berthollet, the dark colour is owing to separation of oxide of silver. (Statique Chimique, vol. i. p. 195.)

Prop.—It is insoluble in water, and is dissolved very sparingly by the strongest acids; but it is soluble in ammonia. Hyposulphurous acid likewise dissolves it. At a temperature of about 500° it fuses, and forms a semitransparent horny mass on cooling, which has a density of 5·524. It bears any degree of heat, or even the combined action of pure charcoal and heat, without decomposition; but hydrogen gas decomposes it readily with formation of hydrochloric acid. Its eq. is 143·42; symb. $Ag + Cl$, or $AgCl$.

Iodide of Silver.—This compound is formed when iodide of potassium is mixed with a solution of nitrate of oxide of silver. It is of a greenish-yellow colour, and is insoluble in water and ammonia. A film of this compound on the surface of a polished plate of silver, constitutes the substance which receives the impressions of light in Daguerré's beautiful invention of the Daguerréotype.

Its eq. is 234·3; symb. $Ag + I$, or AgI.

Sulphuret of Silver.—Silver has a strong affinity for sulphur. This metal tarnishes rapidly when exposed to an atmosphere containing hydrosulphuric acid gas, owing to the formation of a sulphuret. On transmitting a current of this gas through a solution of lunar caustic, a dark brown precipitate subsides, which is a sulphuret of silver. The *silver glance* of mineralogists is a similar compound, and the same sulphuret may be prepared by heating thin plates of silver with alternate layers of sulphur. This sulphuret is remarkable for being soft and even malleable.

Its eq. is 124·1; symb. $Ag + S$, or AgS.

Silver unites also by the aid of heat with phosphorus, forming a soft, brittle, crystalline compound.

SECTION XXV.

GOLD.

Hist. and Prep.—Gold appears to have been known to the earliest races of man, and to have been esteemed by them as much as by the moderns. It has hitherto been found only in the metallic state, either pure or in combination with other metals. It occurs massive, capillary, in grains, and crystallizes in octohedrons and cubes, or their allied forms. It is sometimes found in primary mountains; but more frequently in alluvial depositions, especially among sand in the beds of rivers, having been washed by water out of disintegrated rocks in which it originally existed. There are few countries in which gold washings have not formerly existed; but the principal supply of gold is from South America, from the gold mines of Hungary, and from the Uralian mountains of Siberia, especially on the Asiatic side of the chain, where separate masses in sand have been found weighing 18 or 20 pounds. Rich deposits of gold appear also to exist in some of the southern provinces of North America. Gold is generally separated from accompanying impurities by the process of amalgamation, similar to that described in the last section; by which means it is freed from iron and all associated metals, excepting silver. In Hungary the gold is purified by cupellation. The silver, which in variable quantity is present in native gold, may be brought into view by dissolving the gold in nitro-hydrochloric acid. The best mode of separation consists in fusing the gold with so much silver that the former may constitute one-fourth of the mass: nitric acid will then dissolve all the silver, and leave the gold. The silver may also be removed by digestion in sulphuric acid.

Prop.—Gold is the only metal which has a yellow colour, a character by which it is distinguished from all other simple metallic bodies. It is capable of receiving a high lustre by polishing, but is inferior in brilliancy to steel, silver, and mercury. In ductility and malleability it exceeds all other metals; but it is surpassed by several in tenacity. Its density is 19·3; when pure it is exceedingly soft and flexible; and it fuses according to Daniell at 2016°.

Gold may be exposed for ages to air and moisture without change, nor is it oxidized by being kept in a state of fusion in open vessels. When intensely ignited by means of electricity or the oxy-hydrogen blowpipe, it burns with a greenish-blue flame, and is dissipated in the form of a purple powder, which is supposed to be an oxide.

Gold is not oxidized or dissolved by any of the pure acids; for it may be boiled even in nitric acid without undergoing any change. Its best solvents are chlorine and nitro-hydrochloric acid; and it appears from the observations of Davy that chlorine is the agent in both cases, since nitro-hydrochloric acid does not dissolve gold, except when it gives rise to the formation of chlorine. It is to be inferred, therefore, that the chlorine unites directly with the gold. It is also readily attached by fluorine.

The most convenient method of dissolivng it is to digest fragments of the metal in a mixture composed of two measures of hydrochloric and one of nitric acid, until the acid is saturated. The excess of acid is then expelled by evaporating the orange-coloured solution until a ruby-red liquid remains, which is the neutral terchloride of gold. On adding water, the chloride is dissolved, forming a solution of a gold-yellow colour.

The eq. of gold, estimated from the analysis of the terchloride by Berzelius, is 199·2; its symb. is Au. The composition of its compounds described in this section is as follows:—

	1 eq. of Gold.			Equiv.	Formulæ.
Protoxide	199·2	+ Oxygen	8	1 eq. =207·2	$Au+O$ or AuO.
Binoxide	199·2	+ do.	16	2 eq. =115·2	$Au+2O$ or AuO_2.
Peroxide	199·2	+ do.	24	3 eq. =123·2	$Au+3O$ or AuO_3.
Protochloride	199·2	+ Chlorine	35·42	1 eq. =234·62	$Au+Cl$ or $AuCl$.
Terchloride	199·2	+ do.	106·26	3 eq. =305·46	$Au+3Cl$ or $AuCl_3$.
Protiodide	199·2	+ Iodine	126·3	1 eq. =325·5	$Au+I$ or AuI.
Teriodide	199·2	+ do.	378·9	3 eq. =578·1	$Au+3I$ or AuI_3.
Tersulphuret	199·2	+ Sulphur	48·3	3 eq. =247·5	$Au+3S$ or AuS_3.

Protoxide of Gold.—It is obtained by the action of a cold solution of potassa on the protochloride of gold, and is separated as a green precipitate, which is partially soluble in the alkaline solution. It spontaneously changes soon after its preparation into metallic gold and the peroxide.

Its eq. is 207·2; symb. $Au+O$, $\dot{Au}$, or AuO.

The *binoxide* is supposed to be the purple oxide which is formed by the combustion of gold; but its composition has not been demonstrated by analysis.

Peroxide.—Prep.—This, the only well-known oxide of gold, is prepared by the action of alkalies on the terchloride, but is obtained quite pure with difficulty. Pelletier recommends that it should be formed by digesting a solution of the terchloride with pure magnesia, washing the precipitate with water, and removing the excess of magnesia by dilute nitric acid. It is apt, however, to retain magnesia, and I am informed by Wagner, of Pesth in Hungary, that the most certain mode of procuring the peroxide is the following. Dissolve one part of gold in the usual way, render it quite neutral by evaporation, and redissolve in 12 parts of water: to the solution add one part of carbonate of potassa dissolved in twice its weight of water, and digest at about 170°. Carbonic acid gradually escapes, and the hydrated peroxide of a brownish-red colour subsides. After being well washed it is dissolved in colourless nitric acid of specific gravity 1·4, and the solution decomposed by admixture with water. The hydrated peroxide is thus obtained quite pure, and is rendered anhydrous by a temperature of 212°.

Prop.—Yellow in the state of hydrate, and nearly black when anhydrous, is insoluble in water, and completely decomposed by solar light or a red heat. Hydrochloric acid dissolves it readily, yielding the common solution of gold; but it forms no definite compound with any acid which contains oxygen. It may indeed be dissolved by nitric and sulphuric acids; but the affinity is so slight that the oxide is precipitated by the addition of water. It combines, on the contrary, with alkaline bases, such as potassa and baryta, apparently forming regular salts, in which it acts the part of a weak acid. This property, which constitutes the difficulty of procuring peroxide of gold quite pure, induced Pelletier to deny that the peroxide of gold is a salifiable base, and to propose for it the name of *auric acid*, its compounds with alkalies being called *aurates*. (An. de Ch. et Ph. xv.)

When recently precipitated peroxide of gold is kept in strong ammonia for about a day, a detonating compound of a deep olive colour is generated, analogous to the fulminating silver described in the last section. According to the analysis of Dumas, its elements are in the ratio of 1 eq. of gold, 2 of nitrogen, 6 of hydrogen, and 3 of oxygen, as expressed by the symbols $Au + N_2 + H_6 + O_3$. With regard to the mode in which these elements are arranged, different opinions may be formed. Dumas thinks the real combination is indicated by the formula $AuN_2 + NH_3 + 3HO$, being a hydrated nituret of gold united with ammonia; but it appears more simple to consider it as a di-aurate of ammonia, expressed by the formula $AuO_3 + 2NH_3$. Its detonation should give rise to metallic gold, water, nitrogen, and ammonia. A similar compound is obtained, and this is the ordinary mode of procuring fulminating gold, by digesting terchloride of gold with an excess of ammonia: a yellow precipitate subsides, the fulminating ingredient of which appears identical with that above described; but a subchloride of gold and ammonia falls at the same time, and adheres so obstinately that it cannot be wholly removed by boiling water. Fulminating gold may be dried at 212°; but friction, or a heat suddenly raised to about 290° or upwards, produces a violent detonation. It is best to make it in small quantities at a time, and to dry it in the open air. (An. de Ch. et Ph. xliv. 167.)

Its eq. is 123·2; symb. $Au + 3O$, $\dddot{Au}$, or AuO_3.

Chlorides of Gold.—On concentrating the solution of gold to a sufficient extent by evaporation, the terchloride may be obtained in ruby-red prismatic crystals, which are very fusible. It deliquesces on exposure to the air, and is dissolved readily by water without residue. It is also soluble in alcohol and ether; and the latter withdraws it from the aqueous solution. It begins to lose chlorine at a temperature of about 400°, being changed into a brown dry mass, which is a mixture of the protochloride and terchloride, soluble in water. At about 600° the terchloride is completely resolved into the yellow insoluble protochloride, which by boiling in water is changed into metallic gold and the soluble terchloride. At a red heat the protochloride loses its chlorine altogether, and metallic gold remains. Its eq. is 234·62; symb. $Au + Cl$, or $AuCl$.

The terchloride of gold is the usual and most convenient form of obtaining a solution of gold and examining its properties in that state. On adding to the solution sulphate of protoxide of iron, a brown precipitate ensues, which is gold in very fine division, and the solution contains sesquisulphate of peroxide and perchloride of iron. The action is such that

6 eq. Sulphate of Protoxide of Iron . . . $6\,(FeO, SO_3.)$

and 1 eq. Terchloride of Gold . . . $Au\,Cl_3$.

yield

2 eq. Sesquisulphate of Peroxide of Iron . . $2(Fe_2O_3, 3SO_3.)$

1 eq. Perchloride of Iron, Fe_2Cl_3, and 1 eq. of Gold . Au.

The precipitate when duly washed with dilute hydrochloric acid, in order to separate adhering iron, is gold in a state of perfect purity. A similar reduction is effected by most of the metals, and by sulphurous and phosphorous acids, and by oxalic acid with escape of carbonic acid gas. When a piece of charcoal is immersed in a solution of gold, and exposed to the direct solar rays, its surface acquires a coating of metallic gold; and ribands may be gilded by moistening them with a dilute solution of gold, and exposing them to a current of hydrogen or phosphuretted hydrogen gas. When a strong aqueous solution of gold is shaken in a phial with an equal volume of pure ether, two fluids result, the lighter of which is an ethereal solution of gold. From this liquid flakes of metal are deposited on standing, especially by exposure to light, and substances moistened with it receive a coating of metallic gold.* The reduction in most of these instances is owing to the chlorine quitting the gold in obedience to some stronger attraction: metals deprive it directly of its chlorine; and deoxidizing agents do so indirectly by combining with the oxygen of water, while its hydrogen acts on the chlorine.

When protochloride of tin is added to a dilute aqueous solution of gold, a purple-coloured precipitate, called the *purple of Cassius*, is thrown down; and the same substance may be prepared by fusing together 150 parts of silver, 20 of gold, and 35·1 of tin, and acting on the alloy with nitric acid, which dissolves out the silver and leaves a purple residue, containing the tin and gold which were employed. To prevent the oxidation of the tin during fusion, the three metals should be projected into a red-hot black-lead crucible, which contains a little melted borax. When the powder of Cassius is fused with vitreous substances, such as flint-glass, or a mixture of sand and borax, it forms with them a purple enamel, which is employed in giving pink colours to porcelain. The essential cause of the colour is probably a compound of the purple or supposed binoxide of gold with earthy matters, similar to the enamel formed by glass and oxide of silver; the oxide of tin is not essential, since finely divided metallic gold alone will give the same tint of purple. Fuchs has shown that the purple of Cassius is best prepared by means of sesquioxide of tin dissolved in hydrochloric acid.

The chemical nature of the purple of Cassius is very obscure.

---

* With respect to the revival of gold from its solutions, the reader may consult an Essay on Combustion, by Mrs. Fulhame, and a paper by Count Rumford, in the Philosophical Transactions for 1798.

From its formation by protochloride of tin it is inferred to contain peroxide of tin and gold either in the metallic state or oxidized to a degree inferior to the peroxide. According to Berzelius its sole loss when heated to redness is 7·65 per cent. of water, and the residue has a brick-red colour arising from a mechanical mixture of metallic gold and peroxide of tin, a statement which is confirmed by Gay-Lussac. (An. de Ch. et Ph. xlix. 396.) The proportion of these products corresponds to 5 equivalents of peroxide of tin, 1 of gold, and 6 of water. Nevertheless, the purple of Cassius, as is indicated both by its colour and its solubility in ammonia, is not a mechanical mixture of these ingredients; nor can it well be regarded as a chemical compound of gold and peroxide of tin, since no definite compound of the kind is known to chemists. The more probable supposition is, that it is a hydrated double salt, composed of peroxide of tin as the acid, united with protoxide of tin and binoxide of gold as bases, in such proportion that the oxygen of the gold exactly suffices to convert the protoxide into peroxide of tin. A compound of this nature is expressed by the formula $2(SnO, SnO_2) + (AuO_2, SnO_2) + 6HO$.

Its eq. is 305·46; symb. $Au + 3Cl$, or $AuCl_3$.

Sulphuret of Gold.—On transmitting a current of hydrosulphuric acid gas through a solution of gold, a black precipitate is formed, which is a sulphuret. It is resolved by a red heat into gold and sulphur.

Its eq. is 247·5; symb. $Au + 3S$, or AuS_3.

The compounds of gold with the other non-metallic bodies have been little examined.

Iodides of Gold.—These compounds have recently been studied by Johnston (Phil. Mag. and An. ix. 266.) The protiodide falls as a greenish yellow powder, when iodide of potassium is added in excess to a solution of the terchloride of gold. Though insoluble in water, it dissolves in a dilute hot solution of iodide of potassium, from which it crystallizes on cooling in golden yellow scales with triangular and square faces. These crystals generally contain about 12 per cent. of metallic gold mechanically mixed with them. They gradually lose iodine at common temperatures, freely at 150°, and are almost wholly decomposed at 230°.

Its eq. is 325·5; symb. $Au + I$, or AuI.

The teriodide is formed when terchloride of gold is added to a solution of iodide of potassium. It falls as a dark green precipitate, which is insoluble in water, but is soluble in hydriodic acid and in solutions of the iodides of potassium and sodium. It is very prone to decomposition from the easy loss of iodine. It is a haloid acid, and forms crystallizable compounds with haloid bases. Thus, on setting aside the solution formed by digesting it in iodide of potassium, the auro-iodide of potassium is deposited in dark brownish red, nearly black needles. These crystals are anhydrous, are more stable than the teriodide, and may be dried at 100° without decomposition. The corresponding salt of sodium is deliquescent. Its eq. is 578·1; symb. $Au + 3I$, or AuI_3.

SECTION XXVI.

PLATINUM.

Hist.—THIS valuable metal occurs only in the metallic state, associated or combined with various other metals, such as copper, iron, lead, titanium, chromium, gold, silver, palladium, rhodium, osmium, and iridium. It has hitherto been found chiefly in Brazil, Peru, and other parts of South America, in the form of rounded or flattened grains of a metallic lustre and white colour, mixed with sand and other alluvial depositions. The particles rarely occur so large as a a pea; but they are sometimes larger, and a specimen brought from South America by Humboldt was rather larger than a pigeon's egg, and weighed 1088·6 grains. In the year 1826, however, Boussingault discovered it in a syenitic rock in the province of Antioquia in South America, where it occurs in veins associated with gold. Rich mines of gold and platinum have also been discovered in the Uralian Mountains. (Edinburgh Journal of Science, v. 323.)

Prop.—Pure platinum has a white colour very much like silver, but of inferior lustre. It is the heaviest of known metals, its density after forging being about 21·25, and 21·5 in the state of wire. Its malleablity is considerable, though far less than that of gold and silver. It may be drawn into wires, the diameter of which does not exceed the 2000th part of an inch. It is a soft metal, and like iron admits of being welded at a high temperature. Wollaston * observed that it is a less perfect conductor of heat than several other metals.

---

* The reader will find, in the Philosophical Transactions for 1829, some important directions by Dr. Wollaston, both as to the mode of extracting platinum from its ores,

Platinum undergoes no change from the combined agency of air and moisture; and it may be exposed to the strongest heat of a smith's forge without suffering either oxidation or fusion. On heating a small wire of it by means of galvanism or the oxy-hydrogen blowpipe, it is fused, and afterwards burns with the emission of sparks. Smithson Tennant showed that it is oxidized when ignited with nitre (Phil. Trans. 1797); and a similar effect is occasioned by pure potassa and lithia. It is not attacked by any of the pure acids. Its solvents are chlorine or solutions, such as nitro-hydrochloric acid, which supply chlorine; and it is dissolved with greater difficulty than gold.

The remarkable property observed by Döbereiner in spongy platinum of causing the union of oxygen and hydrogen gases, was formerly mentioned; a property which Dulong and Thenard showed to be also possessed, though in a lower degree, by platinum in its compact form of wire or foil, and by several other metals. (An. de Ch. et Ph. xxiii. and xxiv.) Faraday (Phil. Trans. 1834, part i.) has lately discussed, with his wonted ability and success, both the conditions required for the effective action of platinum, and the cause of the phenomenon. The sole conditions are purity of the gases and perfect cleanliness of the platinum. By cleanliness is meant perfect absence of foreign matter, pure water excepted; and this condition is easily secured by fusing pure potassa on its surface, washing off the alkali by pure water, then dipping the platinum in hot oil of vitriol, and again washing with water. In this state platinum foil acts so rapidly at common temperatures on oxygen and hydrogen gases mixed in the ratio of 1 to 2, that it often becomes red hot and kindles the mixture. Handling the platinum, wiping it with a towel, or exposing it to the atmosphere for a few days, suffices to soil the surface of the metal, and thereby diminish or prevent its action. These phenomena are supposed to result from the concurring influence of two forces, the self-repulsive energy of similar gaseous particles, and the adhesive attraction exerted between them and the platinum. Each gas, repulsive to itself and not repelled by the platinum, comes into the most intimate contact with that metal, and both gases are so condensed upon its surface that they are brought within the sphere of their mutual attraction and combine. Faraday has given several instances,

---

and of communicating to the pure metal its highest degree of malleability. The essay receives additional interest from being one of those which were composed during the last illness of this truly illustrious philosopher.

similar to those which I had occasion to describe some years ago (Jameson's Journal, xi. 99 and 311), where the action of platinum is retarded or altogether prevented by small quantities of certain gases, such as hydrosulphuric acid, carbonic oxide, and olefiant gases. One would be tempted to suppose that these gases act by soiling the metallic surface, though in some respects this explanation is not satisfactory.

When solutions of platinum are heated with various deoxidizing agents, such as formic acid, formiates, alcohol with alkalies, &c., or when an alloy of zinc and platinum is acted on by nitric acid, platinum is obtained as a finely divided black powder, which absorbs oxygen without chemically combining with it, and transfers it to combustible substances, thus indirectly acting as a powerful oxidizing agent. In this way alcohol and pyroxylic spirit may be converted into acetic and formic acids, sulphurous acid into sulphuric acid, &c. (Döbereiner.)

The eq. of platinum, deduced by Berzelius from the analysis of the bichloride, is 98·8; its symb. is Pt. The composition of its compounds described in this section is as follows:—

	Platinum.				Equiv.	Formulæ.
Protoxide	98·8	1 eq.+Oxygen	8	1 eq. =	106·8	$Pt+O$ or PtO.
Binoxide	98·8	1 eq.+ . .	16	2 eq. =	114·8	$Pt+2O$ or PtO_2.
Sesquioxide?	197·6	2 eq.+ . .	24	3 eq. =	221·6	$2Pt+3O$ or Pt_2O_3.
Protochloride	98·8	1 eq.+Chlorine	35·42	1 eq. =	134·22	$Pt+Cl$ or $PtCl$.
Bichloride	98·8	1 eq.+ . .	70·84	2 eq. =	169·64	$Pt+2Cl$ or $PtCl_2$.
Protiodide	98·8	1 eq.+Iodine	126·3	1 eq. =	225·1	$Pt+I$ or PtI.
Biniodide	98·8	1 eq.+ . .	252·6	2 eq. =	351·4	$Pt+2I$ or PtI_2.
Protosulphuret	98·8	1 eq.+Sulphur	16·1	1 eq. =	114·9	$Pt+S$ or PtS.
Bisulphuret	98·8	1 eq.+ . .	32·2	2 eq. =	131·0	$Pt+2S$ or PtS_2.

Protoxide of Platinum.—This oxide is prepared by digesting protochloride of platinum in a solution of pure potassa, avoiding a large excess of the alkali, since it dissolves a portion of the oxide and thereby acquires a green colour. In this state it is a hydrate which loses first its water and then oxygen when heated, and dissolves slowly in acids, yielding solutions of a brownish-green tint.

Its eq. is 106·8; symb. $Pt + Cl$, $\dot{Pt}$, or PlO.

Binoxide.—This oxide is prepared with difficulty, owing to its disposition, like peroxide of gold, to act rather as an acid than an alkaline base, and either to fall in combination with any alkali by which it is precipitated, or to remain with it altogether in solution. Berzelius recommends that it should be prepared by exactly decomposing sulphate of binoxide of platinum with nitrate of baryta, and adding pure soda to the filtered solution, so as to precipitate about half of the oxide; since otherwise, a sub-salt would subside. The oxide falls in the form of a bulky hydrate, of a yellowish-brown colour: it resembles rust of iron when dry, and is nearly black when rendered anhydrous.

Its eq. is 114·8: symb. $Pt + 2O$, $\ddot{Pt}$, or PtO_2.

Sesquioxide.—This oxide, of a grey colour, is prepared, according to its discoverer Mr. E. Davy, by heating fulminating platinum with nitrous acid; but the nature of the compound so formed has not yet been decisively determined. (Phil. Trans. 1820.)

Protochloride.—When the bichloride is heated to 450°, half of its chlorine is expelled, and the protochloride of a greenish-grey colour remains. It is insoluble in water, sulphuric acid, and nitric acid; but hydrochloric acid partially dissolves it, yielding a red solution. At a red heat its chlorine is driven off, and metallic platinum is left. It is dissolved by a solution of the bichloride.

Its eq. is 134·22; symb. $Pt + Cl$, or $PtCl$.

Bicholoride of Platinum.—This chloride is obtained by evaporating the solution of platinum in nitro-hydrochloric acid to dryness at a very gentle heat, when it remains as a red hydrate, which becomes brown when its water is expelled. It is deliquescent, and very soluble in water, alcohol, and ether; its solution, if free from the chlorides of palladium and iridium, being of a pure yellow colour. Its ethereal solution is decomposed by light, metallic platinum being deposited.

A solution of platinum is recognized by the following characters. When to an alcoholic or concentrated aqueous solution of the bichloride a solution of chloride of potassium is added, a crystalline double chloride of a pale yellow colour subsides, which is insoluble in alcohol, and sparingly soluble in water: at a red heat it yields chlorine gas, and the residue consists of metallic platinum and chloride of potassium. With a solution of hydrochlorate of ammonia a similar yellow salt falls, which when ignited leaves pure platinum in the form of a delicate spongy mass, the power of which in kindling an explosive mixture of oxygen and hydrogen gases has already been mentioned.

Its eq. is 169·64; symb. $Pt + 2Cl$, or $PtCl_2$.

Protiodide of Platinum.—Lassaigne prepared this compound by digesting the protochloride of platinum in a rather strong solution of iodide of potassium, when the protiodide gradually appeared in the form of a black powder, which is insoluble in water and alcohol.

It is unchanged by the sulphuric, nitric, and hydrochloric acids, decomposed by the alkalies, and at a red heat gives off its iodine. Its eq. is 225·1; symb. $Pt + I$, or PtI.

Periodide of Platinum.—Lassaigne prepares this compound by the action of iodide of potassium on a rather dilute solution of bichloride of platinum. At first the liquid acquires an orange-red and then a claret colour, without any precipitation; but when the solution is boiled a black precipitate subsides, which should be washed with hot water and dried at a heat not exceeding 212°. This biniodide is a black powder, sometimes crystalline, is tasteless and inodorous, insoluble in water, and may be boiled in water without change. By alcohol it is sparingly dissolved, especially when heated. Acids act feebly upon it; but it is decomposed by alkalies, and begins to lose iodine at 270°. (An. de Ch. et Ph. li. 113.) Its eq. is 351·4; symb. $Pt + 2I$, or PtI_2.

Protosulphuret of Platinum.—It is formed by heating in a retort the yellow ammoniacal chloride of platinum with half its weight of sulphur until all the sal-ammoniac and excess of sulphur is expelled. The protosulphuret is then left as a grey powder of a metallic lustre. It may also be formed by the action of hydrosulphuric acid on protochloride of platinum.

Its eq. is 114·9; symb. $Pt + S$, or PtS.

Bisulphuret.—It is formed as a brown precipitate, which becomes black when dried, by letting fall a solution of bichloride of platinum drop by drop into a solution of sulphuret of potassium, or by transmitting hydrosulphuric acid gas into a solution of the double chloride of platinum and sodium. (Berzelius.) It should be dried in vacuo by aid of sulphuric acid, since by exposure to the air in a moist state sulphuric acid is generated.

Its eq. is 130; symb. $Pt + 2S$, or PtS_2.

Fulminating platinum may be prepared by the action of ammonia in slight excess on a solution of sulphate of oxide of platinum. (E. Davy.) It is analogous to the detonating compounds which ammonia forms with the oxides of gold and silver.

SECTION XXVII.

PALLADIUM.—RHODIUM.—OSMIUM.—IRIDIUM.

The four metals to be described in this section are all contained in the ore of platinum, and have hitherto been procured in very small quantity. When the ore is digested in nitro-hydrochloric acid, the platinum, together with palladium, rhodium, iron, copper, and lead, is dissolved; while a black powder is left consisting of osmium and iridium, mixed in general with a considerable quantity of titanate of iron, and siliceous minerals.

PALLADIUM.

Hist. and Prep.—Discovered in 1803 by Wollaston (Phil. Trans. 1804 and 1805). On adding bicyanuret of mercury dissolved in water to a neutral solution of the ore of platinum, either before or after the separation of that metal by hydrochlorate of ammonia, a yellowish-white flocculent precipitate is gradually deposited, which is cyanuret of palladium. When this compound is heated to redness, the cyanogen is expelled, and pure palladium remains. In order to obtain it in a malleable state, the metal should be heated with sulphur, and the resulting sulphuret purified by cupellation in an open crucible with borax and a little nitre. It is then roasted at a low red heat on a flat brick, and when reduced to a pasty consistence, it is pressed into a square or oblong perfectly flat cake. It is again to be roasted very patiently, at a low red heat, until it becomes spongy on the surface; and when quite cold, it is condensed by frequent tappings with a light hammer. By alternate roastings and tappings the sulphur is burned off, and the metal rendered sufficiently dense to be laminated. Thus prepared it is rather brittle while hot, which Wollaston supposed to arise from a small remnant of sulphur. (Phil. Trans. 1829, p. 7.)

Prop.—It resembles platinum in colour and lustre. It is ductile as well as malleable, and is considerably harder than platinum. Its sp. gr. varies from 11·3 to 11·8. In fusibility it is intermediate between gold and platinum, and is dissipated in sparks when intensely heated by the oxy-hydrogen blowpipe. At a red heat in oxygen gas its surface acquires a fine blue colour, owing to superficial oxidation; but the increase of weight is so slight as not to be appreciated. It is oxidized and dissolved by nitric acid, and even the sulphuric and hydrochloric acids act upon it by the aid of heat; but its proper solvent is nitro-hydrochloric acid. Its oxide forms beautiful red-coloured salts, from which metallic palladium is precipitated by sulphate of protoxide of iron, and by all the metals described in the foregoing sections, excepting silver, gold, and platinum.

From the analysis by Berzelius of the double chloride of palladium and potassium the eq. of palladium is inferred to be 53·3. Its symb. is Pd. The composition of its compounds described in this section is as follows:—

	Palladium.				Equiv.	Formulæ.
Protoxide	53·3	1 eq.+Oxygen	8	1 eq.=	61·3	Pd+O or PdO.
Binoxide	53·3	1 eq.+do.	16	2 eq.=	69·3	Pd+2O or PdO_2.
Protochloride	53·3	1 eq.+Chlorine	35·42	1 eq.=	88·72	Pd+Cl or PdCl.
Bichloride	53·3	1 eq.+do.	70·84	2 eq.=	124·14	Pd+2Cl or $PdCl_2$.
Protosulphuret	53·3	1 eq.+Sulphur	16·1	1 eq.=	69·4	Pd+S or PdS.

Protoxide of Palladium.—This oxide is obtained as a hydrate of a deep brown colour by decomposing its salts with an excess of carbonate of potassa or soda; and, by washing and heating to low redness, the anhydrous protoxide of a black colour is left. It is also obtained by heating the nitrate at a low red heat. In the anhydrous state it is dissolved with difficulty by acids. When strongly heated it parts with its oxygen. Berzelius says it falls from its salts on the addition of the alkalies as a sub-salt, which is dissolved by the alkali in excess.

Its eq. is 61·3; symb. Pd + O, $\dot{\mathrm{P}}\mathrm{d}$, or PdO.

Binoxide.—To prepare this oxide Berzelius recommends that a solution of potassa or its carbonate in excess should be poured by little and little on the *solid* bichloride of palladium and potassium, and the materials be well intermixed: water is not first added, because it decomposes the double chloride; and the alkali is not added all at once, because the binoxide would then be dissolved at first, and afterwards separate out as a gelatinous hydrate, which could not be purified by washing. When prepared with the foregoing directions, the binoxide is obtained as a hydrate of a deep yellowish-brown colour, which retains a little potassa in combination; but on heating the solution to 212° the alkali is dissolved, and the anhydrous black oxide left.

Its eq. is 69·3; symb. Pd + 2O, $\ddot{\mathrm{P}}\mathrm{d}$, or PdO_2.

Protochloride of Palladium.—It is obtained by evaporating to dryness a solution of palladium in nitro-hydrochloric acid, being left as a brown crystalline hydrate, which becomes black when its water is expelled. It loses its chlorine when strongly heated, and is soluble in water. Its eq. is 88·72; symb. $Pd + Cl$, or $PdCl$.

The *bichloride* is formed by digesting the protochloride in nitro-hydrochloric acid, and exists only in solution, the colour of which is of so deep a brown as to appear nearly black. It is readily distinguished from the protochloride by yielding with chloride of potassium a double chloride of a red colour; whereas that formed with the protochloride is yellow.

Its eq. is 124·14; symb. $Pd + 2Cl$, or $PdCl_2$.

Protosulphuret of Palladium.—It is readily formed by heating the metal with sulphur, and is a fusible brittle compound of a grey colour. Its eq. is 69·4; symb. $Pd + S$, or PdS.

RHODIUM.

Hist. and Prep.—This metal was discovered by Wollaston at the time he was occupied with the discovery of palladium. On immersing a thin plate of clean iron into the solution from which palladium and the greater part of the platinum have been precipitated, the rhodium, together with small quantities of platinum, copper, and lead, is thrown down in the metallic state; and on digesting the precipitate in dilute nitric acid, the two last metals are removed. The rhodium and platinum are then dissolved by means of nitro-hydrochloric acid, and the solution, after being mixed with some chloride of sodium, is evaporated to dryness. Two double chlorides result, that of platinum and sodium, and of rhodium and sodium, the former of which is soluble, and the latter insoluble in alcohol; and they may therefore be separated from each other by this menstruum. The double chloride of rhodium is then dissolved in water, and metallic rhodium precipitated by insertion of a rod of zinc.

Prop.—Thus procured, it is in the form of a black powder, which requires the strongest heat that can be produced in a wind furnace for fusion, and when fused has a white colour and metallic lustre. It is brittle, is extremely hard, and has a sp. gr. of about 11. It attracts oxygen at a red heat, a mixture of peroxide and protoxide being formed. It is not attacked by any of the acids when in its pure state; but if alloyed with other metals, such as copper or lead, it is dissolved by nitro-hydrochloric acid, a circumstance which accounts for its presence in the solution of crude platinum. It is oxidized by being ignited either with nitre, or bisulphate of potash. When heated with the latter, sulphurous acid gas is evolved, and a double sulphate of peroxide of rhodium and potash is generated, which dissolves readily in hot water, and yields a yellow solution. The presence of rhodium in platinum, iridium, and osmium may thus be detected, and by repeated fusion a perfect separation be accomplished. (Berzelius.)

Chemists are acquainted with two oxides of rhodium. The protoxide is black, and the peroxide, which is the base of the salts of rhodium, is of a yellow colour. Most of its salts are either red or yellow.

From the composition of the double chloride of rhodium and potassium Berzelius considers 52·2 as the eq. of rhodium; its symb. is R, and its compounds described in this section are thus constituted:—

	Rhodium.			Equiv.	Formulæ.
Protoxide	52·2	1 eq.+Oxygen	8	1 eq.= 60·2	$R+O$ or RO.
Peroxide	104·4	2 eq.+do.	24	3 eq.=128·4	$2R+3O$ or R_2O_3.
Protochloride	52·2	1 eq.+Chlorine	35·42	1 eq.= 87·62	$R+Cl$ or RCl.
Perchloride	104·4	2 eq.+do.	106·26	3 eq.=210·66	$2R+3Cl$ or R_2Cl_3.
Sulphuret.	Probably a protosulphuret.				

Oxides of Rhodium.—The first grade of oxidation has not yet been insulated. The peroxide is generated when pulverulent rhodium is heated to redness in a silver crucible mixed with hydrate of potassa and a little nitre, when the rhodium is oxidized and acquires a coffee-brown colour. To remove the potassa united with the peroxide, the mass is first washed with water and then digested in hydrochloric acid, when it acquires a greenish-grey colour, and is left as a pure hydrate of the peroxide. In this state it is insoluble in acids. If an excess of carbonate of potassa or soda is added to the double chloride of rhodium and potassium, and the solution is evaporated, a gelatinous hydrate falls; but on attempting to dissolve in acid the potassa combined with the peroxide, the latter is also dissolved.

Its eq. is 128·4; symb. $2R+3O$, $\overset{\cdots}{\underline{R}}$, or R_2O_3.

Chlorides of Rhodium.—The only chloride which has yet been insulated is the perchloride, which Berzelius obtained by adding to a solution of the double chloride of rhodium and potassium silicohydrofluoric acid as long as the double fluoride of potassium and silicon was generated, after which the filtered liquid was evaporated to dryness, and redissolved in water. This perchloride when dry has a dark brown colour, is uncrystalline, and decomposed by a full red heat into chlorine and metallic rhodium. It deliquesces in the air into a brown liquid, and its aqueous solution has a fine red colour, whence its name of rhodium (from *ῥοδον*, a rose) is derived. (An. de Ch. et Ph. xl. 51.)

Its eq. is 210·66; symb. $2R + 3Cl$, or R_2Cl_3.

Sulphuret of Rhodium.—It may be formed by heating rhodium directly with sulphur, fuses at a white heat without decomposition, and has a bluish-grey colour, with a metallic lustre. Wollaston made use of it for procuring the metal in a coherent state, in the same manner as sulphuret of palladium.

IRIDIUM AND OSMIUM.

Hist.—These metals were discovered by the late Mr. Tennant in the year 1803 (Phil. Trans. 1804), and the discovery of iridium was made about the same time by Descotils in France. The black powder mentioned at the beginning of this section is a compound of iridium and osmium, an alloy which Wollaston detected in the form of flat white grains among fragments of crude platinum. This alloy, which is quite insoluble in nitro-hydrochloric acid, is the source from which iridium and osmium are extracted.

Osmium and Iridium.—Prep.—These metals are obtained from the pulverulent residue of the ores of platinum, after that metal together with palladium and rhodium have been removed by digestion in nitro-hydrochloric acid. Wollaston has recommended the following process (Phil. Trans. 1829, p. 8). The residue is ground into a fine powder with a third of its weight of nitre, and the mixture heated to redness in a silver crucible until it is reduced to a pasty state, when the characteristic odour of oxide of osmium will be perceptible. Dissolve the soluble parts, which contain oxide of osmium in combination with potassa, in the smallest possible quantity of water, and acidulate the solution, introduced into a retort, with sulphuric acid diluted with its own weight of water. By distilling rapidly into a clean receiver as long as osmic fumes pass over, the acid will be collected on its sides in the form of a white crust; and, there melting, it will run down in drops beneath the watery solution, forming a fluid flattened globule at the bottom. As the receiver cools, the acid becomes solid and crystallizes. Osmium is precipitated from the solution of its acid by all the metals, excepting gold and silver. A convenient mode of reduction is to agitate it with mercury, adding hydrochloric acid to decompose the protoxide of mercury which is formed, and then expelling the mercury and calomel by heat. The osmium is left as a black porous powder which acquires metallic lustre by friction.

The insoluble parts contain the iridium as oxide in combination with potassa. On digesting the mass in hydrochloric acid, a blue solution is obtained; but it afterwards becomes of an olive-green hue, and subsequently acquires a deep-red tint. This variety of colour, which suggested the name of iridium (Iris, the rainbow), is owing to the successive production of different compounds. The iridium may be precipitated from the solution by any metal except gold and platinum, or it may be obtained by exposing the chloride to a red heat. Wöhler has proposed a very elegant process by which both metals may be obtained on a large scale (Pog. An. xxxi. 161). The great advantage of his method is, that it leaves the titanate of iron and other foreign minerals undecomposed. He mixes the residue with an equal weight of fused sea-salt in fine powder. The mixture is introduced into a long and wide green glass tube, which is connected at one extremity with an apparatus for developing chlorine, at the other with a tubulated receiver. The latter is furnished with a small tube, the extremity of which is made to dip into a weak solution of ammonia. The tube containing the mixture of salt and ore being then brought to a low red heat, the chlorine is developed and the gas transmitted in a moderate stream through the glowing mass, by which in the first part of the process it is abundantly and completely absorbed. The operation is to be continued until the chlorine is observed to pass pretty freely into the solution of ammonia. The changes which occur are owing to the formation of two haloid acids, by the combination of the chlorine with both metals of the ore; and as these instantly combine with the chloride of sodium, two soluble salts, the iridio-chloride of sodium, and the osmio-chloride of sodium, are produced. But by the moisture of the chlorine gas the latter compound is decomposed, the chloride of osmium giving rise to the formation of osmic and hydrochloric acids, and the deposition of a part of the osmium in the metallic state. This by again combining with chlorine gives rise to a repetition of the same changes, and to the production of an additional quantity of osmic acid, which, being volatile, passes on and is deposited in crystals in the receiver.

The solution of ammonia prevents the loss of any acid which might escape condensation. The solid matter in the tube is then digested in water, when a deep brown solution is obtained, and the clear liquid is separated by decantation from the insoluble parts, which consists principally of titanate of iron. As the solution still contains some osmic acid, it is submitted to a distillation until one-half has passed over into a weak solution of ammonia. The remainder is then evaporated in an open dish, while carbonate of soda is at the same time added in successive portions until a considerable excess is present. On evaporating to dryness, a black mass is obtained, which is to be exposed to a low red heat in a hessian crucible. When cold, the saline matter is removed by boiling water, and the sesquioxide of iridium is left in the form of a black powder. It is readily reduced to the metallic state by a stream of hydrogen gas.

Osmium.—As obtained by precipitation it is a black porous powder, which acquires metallic lustre by friction. After exposure to a very gentle heat, its sp. gr. is 7. It takes fire when heated in the open air, and is readily oxidized and dissolved by fuming nitric acid; but a red heat gives it greater compactness, and in that state it ceases to be attacked by acids, and may be freely heated without oxidation. In its densest state Berzelius found its sp. gr. to be 10. (An. de Ch. et Ph. xl. 257, and xlii. 185.) Its symb. is Os.

Berzelius, from his late researches on the compounds of osmium, considers 99·7 to be its eq., and gives the composition of its oxides, chlorides, and sulphurets, as follows:—

	Osmium.			Equiv.	Formulæ.
Protoxide	99·7	1 eq.+Oxygen	8	1 eq.=107·7	Os+O or OsO.
Sesquioxide	199·4	2 eq.+do.	24	3 eq.=223·4	2Os+3O or Os_2O_3.
Binoxide	99·7	1 eq.+do.	16	2 eq.=115·7	Os+2O or OsO_2.
Teroxide	99·7	1 eq.+do.	24	3 eq.=123·7	Os+3O or OsO_3.
Osmic acid	99·7	1 eq.+do.	32	4 eq.=131·7	Os+4O or OsO_4.
Protochloride	99·7	1 eq.+Chlorine	35·42	1 eq.=135·12	Os+Cl or OsCl.
Sesquichlor.	199·4	2 eq.+do.	106·26	3 eq.=205·66	2Os+3Cl or Os_2Cl_3.
Bichloride	99·7	1 eq.+do.	70·84	2 eq.=170·54	Os+2Cl or $OsCl_2$.
Terchloride	99·7	1 eq.+do.	106·26	3 eq.=205·96	Os+3Cl or $OsCl_3$.
Protosulphuret	99·7	1 eq.+Sulphur	16·1	1 eq.=115·8	Os+S or Os or OsS.
Sesquisulph.	199·4	2 eq.+do.	48·3	3 eq.=247·7	2Os+3S or Os_2S_3.
Bisulphuret	99·7	1 eq.+do.	32·2	2 eq.=131·9	Os+2S or OsS_2.
Tersulphuret	99·7	1 eq.+do.	48·3	3 eq.=148·0	Os+3S or OsS_3.

Oxides of Osmium.—For a minute description of these compounds I refer to the essays of Berzelius above cited. The protoxide is precipitated by pure alkalies from the protochloride, and falls as a deep green, nearly black, hydrate, which is soluble in acids, and detonates when heated with combustible matter. The binoxide is thrown down as a hydrate of a deep brown colour, when a saturated solution of the bichloride is heated with carbonate of soda. It retains a little alkali in combination; but the soda is easily removed by dilute hydrochloric acid, without the oxide being dissolved. The teroxide is prepared in like manner from the terchloride. The sesquioxide has not been obtained in a separate state; but it is procured in combination with ammonia when the binoxide is treated with a large excess of pure ammonia, nitrogen gas being disengaged at the same time.

The highest stage of oxidation is the volatile acid, which is the product of the oxidation of osmium by acids, by combustion, or by fusion with nitre or alkalies; and it may be procured by the process above mentioned in colourless transparent elongated crystals, or as a colourless solution in water. Its vapour is very acrid, exciting cough, irritating the eyes, and producing a copious flow of saliva; and its odour is disagreeable and pungent, somewhat like that of chlorine; a property which suggested the name of *Osmium* (from *οσμη*, odour). It does not combine with acids: on the contrary, though it has no acid reaction, it unites with alkalies, and the compound sustains a strong heat without decomposition. When touched, it communicates a stain which cannot be removed by washing. With the infusion of gall-nuts it yields a purple solution, which afterwards acquires a deep blue tint; a character which forms a sure and extremely delicate test for peroxide of osmium. By sulphurous acid it is deoxidized, and the colour of the solution passes through the shades of yellow, orange, brown, green, and lastly blue, when it resembles sulphate of indigo. These changes correspond to sulphates of the different oxides of osmium, the last or blue oxide being a compound of protoxide and sesquioxide of osmium.

Chlorides of Osmium.—Berzelius has described four chlorides of osmium, corresponding to the four first degrees of oxidation above mentioned. When osmium is heated in a tube in a current of dry chlorine gas, a deep green sublimate is formed, which is the protochloride. On continuing the process it yields a red sublimate, which is the bichloride. For the remaining details, which are rather minute, I may refer to the essay already cited. Several of these chlorides yield double compounds with sodium, potassium, and ammonia

Osmium unites with sulphur in the dry way, or when precipitated from the chlorides by hydrosulphuric acid. The sulphurets obviously correspond to the number of the oxides. (Berzelius.)

Iridium.—Prop.—A brittle metal, and apt to fall into powder when burnished; but with care it may be polished, and then acquires the appearance of platinum. Of all known metals it is the most infusible: Children, by means of his large galvanic battery, fused it into a globule of a brilliant metallic lustre and white colour, having a density of 18·68; but the attempts at fusion by Berzelius were unsuccessful. Breithaupt states that the sp. gr. of native iridium, lately found in the Russian mines of platinum, although not quite free from lighter metals, varies from 23 to 26. This would make iridium the heaviest of metals. It is also, according to Breithaupt, the hardest and the most indestructible by acids. Hence, if it could be easily wrought it would be invaluable for the edges of delicate balances. It is oxidized at a red heat in the open air, if in a state of fine division, but not otherwise; and it is attacked with difficulty even by nitro-hydrochloric acid.

The eq. of iridium is estimated by Berzelius at 98·8, being identical with that of platinum. It forms with oxygen four oxides exactly analogous in composition to the four first oxides of osmium in the foregoing table, and its four chlorides correspond to those of osmium. Its sulphurets have been little examined, but they doubtless correspond to the oxides. (An. de Ch. et Ph. xl. 257, and xliii. 185.) Its symb. is Ir.

Oxides of Iridium.—The protoxide, sesquioxide, and teroxide are precipitated by alkalies from the chloride, to which each is respectively proportional. The protoxide is greenish-grey as a hydrate, and black when anhydrous. The sesquioxide is bluish-black in the dry state, and deep brown as a hydrate. The hydrated teroxide is of a yellowish-brown or greenish colour. The binoxide has not hitherto been insulated. Berzelius has not fully decided the nature of the compound which is considered as the blue oxide, that which forms a blue solution with acids; but he believes it to be a compound of the protoxide and sesquioxide. This variety of oxides, together with the facility with which they appear to pass from one to the other, amply accounts for the diversity of tints sometimes observed in solutions of iridium.

Chlorides of Iridium.—The protochloride is obtained as a light powder of a deep olive-green colour, by transmitting chlorine gas over pulverulent iridium heated to a commencing red heat. When heated to redness its chlorine is expelled. It is insoluble in water, and but sparingly dissolved by acids, even the nitro-hydrochloric; but when the hydrated protoxide is digested in hydrochloric acid, the protochloride is reproduced and dissolved, forming probably a soluble compound of the protochloride and hydrochloric acid. Its solution is a mixture of brown, green, and yellow. (Berzelius.)

The *sesquichloride* is best obtained by calcining iridium with nitre, digesting the product in nitric acid, and, after washing, dissolving the residual oxide in hydrochloric acid. Its solution has a dark yellowish-brown tint, which is so intense that a small quantity renders water opaque. By evaporation it yields a black mass, wholly uncrystalline, and deliquescent in the air.

The *bichloride* is formed by digesting at a moderate heat the sesquichloride in nitro-hydrochloric acid. It is deliquescent and very soluble, yielding a solution of a dark reddish-brown colour. When its solution is evaporated to dryness, except at a heat not exceeding 104°, it loses chlorine, and is reconverted into the sesquichloride.

The *terchloride* has not been obtained in a separate form, but only as a double chloride of potassium. It appears to be the principal compound formed in the process above given for extracting iridium from its ore, and is recognized by its rose-red tint.

Iridium has a considerable affinity for carbon, combining with it when a piece of metal is held in the flame of a spirit-lamp. The resulting carburet contains 19·8 per cent. of carbon.

SECTION XXVIII.

ON METALLIC COMBINATIONS.

Having completed the history of the individual metals, and of the compounds resulting from their union with the simple non-metallic bodies, I shall treat briefly in the present section of the combinations of the metals with each other. These compounds are called *alloys;* and to those alloys, of which mercury is a constituent, the term *amalgam* is applied. It is probable that each metal is capable of uniting in one or more proportions with every other metal, and on this supposition the number of alloys would be exceedingly numerous. This department of chemistry, however, owing to its having been cultivated with less zeal than most other branches of the science, is as yet limited, and our knowledge concerning it imperfect. On this account I shall mention those alloys only to which some particular interest is attached.

Metals do not combine with each other in their solid state, owing to the influence of chemical affinity being counteracted by the force of cohesion. It is necessary to liquefy at least one of them, in which case they always unite, provided their mutual attraction is energetic. Thus, brass is formed when pieces of copper are put into melted zinc; and gold unites with mercury at common temperatures by mere contact.

Metals appear to unite with one another in every proportion, precisely in the same manner as sulphuric acid and water. Thus there is no limit to the number of alloys of gold and copper. It is certain, however, that metals have a tendency to combine in definite proportion; for several atomic compounds of this kind occur native. The crystallized amalgam of silver, for example, is composed, according to the analysis of Klaproth, of 64 parts of mercury and 36 of silver; numbers which are so nearly in the ratio of 202 to 108, that the amalgam may be inferred to contain one eq. of each of its elements. It is indeed possible that the variety of proportion in alloys is rather apparent than real, arising from the mixture of a few definite compounds with each other, or with uncombined metal; an opinion not only suggested by the mode in which alloys are prepared, but in some measure supported by observation. Thus, on adding successive small quantities of silver to mercury, a great variety of fluid amalgams are apparently produced; but, in reality, the chief, if not the sole compound, is a solid amalgam, which is merely diffused throughout the fluid mass, and may be separated by pressing the liquid mercury through a piece of thick leather.

This view is strengthened by some late experiments by Rudberg (An. de Ch. et Ph. xlviii. 363). He finds that variable mixtures of metals in cooling after fusion have generally two periods when the thermometer is stationary. In alloys of lead and tin one of these points is uniformly at $368\frac{1}{2}°$ for all mixtures, while the other point varies according as one or the other metal is predominant, and is near the fusing point of the predominating metal. From this it is inferred that the latter point is caused by the congelation of the predominating metal, and the constant point is the congealing temperature of an alloy of uniform composition present in all the mixtures. This alloy is composed of 3 eq. of tin and 1 eq. of lead, its congealing point being 368½°. In variable mixtures of bismuth and tin the constant point is 289½°, which is the congealing temperature of an alloy composed of single eq. of tin and bismuth.

Alloys are analogous to metals in their chief physical properties. They are opaque, possess the metallic lustre, and are good conductors of heat and electricity. They often differ materially in some respects from the elements of which they consist. The colour of an alloy is sometimes different from that of its constituents, of which brass is a remarkable example. The hardness of a metal is in general increased by being alloyed, and for this reason its elasticity and sonorousness are frequently improved. The malleability and ductility of metals, on the contrary, are usually impaired by combination. Alloys formed of two brittle metals are always brittle; and an alloy composed of a ductile and a brittle metal is generally brittle, especially if the latter predominate. An alloy of two ductile metals is sometimes brittle.

The density of an alloy is sometimes less, sometimes greater, than the mean density of the metals of which it is composed.

The fusibility of metals is greatly increased by being alloyed. Thus pure platinum, which cannot be completely fused in the most intense heat of a wind furnace, forms a very fusible alloy with arsenic.

The tendency of metals to unite with oxygen is considerably augmented by being alloyed. This effect is particularly conspicuous when dense metals are liquefied by combination with quicksilver. Lead and tin, for instance, when united with mercury, are soon oxidized by exposure to the atmosphere; and even gold and silver combine with oxygen, when the amalgams of those metals are agitated with air. The oxidability of one metal in an alloy appears in some instances to be increased in consequence of a galvanic action. Thus, Faraday observed that an alloy of steel with 100th of its weight of platinum was dissolved with effervescence in dilute sulphuric acid, which was so weak that it scarcely acted on common steel; an effect which he ascribes to the steel in the alloy being rendered positive by the presence of the platinum. De la Rive has noticed a similar instance in commercial zinc, the oxidability of which is increased by the presence of small quantities of iron. In these cases, however, the effect is due rather to one metal being mechanically enveloped in another than to actual combination.

AMALGAMS.

Quicksilver unites with potassium when agitated in a glass tube with that metal, forming a solid amalgam. When the amalgam is put into water, the potassium is gradually oxidized, hydrogen gas is disengaged, and the mercury resumes its liquid form. A similar compound may be obtained with sodium. These amalgams may also be procured by placing the negative wire in contact with a globule of mercury during the process of decomposing potassa and soda by galvanism.

A solid amalgam of tin is employed in making looking-glasses; and an amalgam made of one part of lead, one of tin, two of bismuth, and four parts of mercury, is used for silvering the inside of hollow glass globes. This amalgam is solid at common temperatures; but it is fused by a slight degree of heat.

The amalgam of zinc and tin, used for promoting the action of the electrical machine, is made by fusing one part of zinc with one of tin, and then agitating the liquid mass with two parts of hot mercury placed in a wooden box. Mercury evinces little disposition to unite with iron, and, on this account, it is usually preserved in iron bottles.

The amalgam of silver, as already mentioned, is a mineral production. The process of separating silver from its ores by amalgamation, practised on a large scale at Freyberg in Germany, is founded on the affinity of mercury for silver. On exposing the amalgam to heat, the quicksilver is volatilized, and pure silver remains.

Gold unites with remarkable facility with mercury, forming a white-coloured compound. An amalgam composed of one part of gold and eight of mercury is employed in gilding brass. The brass, after being rubbed with nitrate of oxide of mercury, in order to give it a thin film of quicksilver, is covered with the amalgam of gold, and then exposed to heat for the purpose of expelling the mercury.

ALLOYS OF ARSENIC.

Arsenic has a tendency to render the metals, with which it is alloyed, both brittle and fusible. It has the property of destroying the colour of gold and copper. An alloy of copper, with a tenth part of arsenic, is so very similar in appearance to silver, that it has been substituted for it. The whitness of this alloy affords a rough mode of testing for arsenic; for if arsenious acid and charcoal be heated between two plates of copper, a white stain afterwards appears upon its surface, owing to the formation of an arseniuret of copper.

The presence of arsenic in iron has a very pernicious effect; for even though in small proportion, it renders the iron brittle, especially when heated.

The alloy of tin and arsenic is employed for forming arseniuretted hydrogen gas by the action of hydrochloric acid. The tin of commerce sometimes contains a minute quantity of this alloy.

An alloy of platinum with ten parts of arsenic is fusible at a heat a little above redness, and may therefore be cast in moulds. On exposing the alloy to a gradually increasing temperature in open vessels, the arsenic is oxidized and expelled, and the platinum recovers its purity and infusibility.

ALLOYS OF TIN, LEAD, ANTIMONY, AND BISMUTH.

Tin and lead unite readily when fused together, constituting solder, of which two kinds are distinguished. The alloy called *fine solder*, consists of two parts of tin and one of lead, fuses at about 360°, and is much employed in tinning copper. The *coarse solder* contains 1-4th of tin, fuses at about 500°, and is the substance used for soldering by glaziers. Thus, by varying the relative quantity of the metals, a solder of different fusibility may be obtained. The process of hard soldering or *brazing*, by which two surfaces of copper are cemented together, is done with *hard solder*, which is made by fusing together brass and zinc: the copper requires to be heated, when this solder is used, to near its point of fusion.

It has been observed by Kupfer that most of the *alloys* of tin and lead, made in atomic proportion, have a sp. gr. less than their calculated density; from which it is manifest that they expand in uniting. The *amalgams* of lead and tin, on the contrary, occupy less space, when combined, than their elements did previously.

Tin alloyed with small quantities of antimony, copper, and bismuth, forms the best kind of pewter. Inferior sorts contain a large proportion of lead.

Tin, lead, and bismuth, form an alloy which is fused at a temperature below 212°. The best proportion, according to D'Arcet, is 8 parts of bismuth, 5 of lead, and 3 of tin.

An alloy of three parts of lead to one of antimony constitutes the substance of which types for printing are made.

A native alloy of antimony and nickel, found at Andreasberg in the Harz, was found by Stromeyer to consist of 29·5 parts or 1 eq. of nickel, and 64·4 parts or 1 eq. of antimony.

ALLOYS OF COPPER.

Copper forms with tin several valuable alloys, which are characterized by their sonorousness. Bronze is an alloy of copper with about eight or ten per cent. of tin, together with small quantities of other metals which are not essential to the compound. Cannons are cast with an alloy of a similar kind.

The best bell-metal is composed of 80 parts of copper and 20 of tin;—the Indian gong, celebrated for the richness of its tones, contains copper and tin in this proportion. A specimen of English bell-metal was found by Dr. Thomson to consists of 80 parts of copper, 10·1 of tin, 5·6 of zinc, and 4·3 of lead. Lead and antimony, though in small quantity, have a remarkable effect in diminishing the elasticity and sonorousness of the compound. *Speculum-metal*, with which mirrors for telescopes are made, consists of about two parts of copper and one of tin. The whiteness of the alloy is improved by the addition of a little arsenic.

Copper and zinc unite in several proportions, forming alloys of great importance in the arts. The best brass consists of four parts of copper to one of zinc; and when the latter is in a greater proportion, compounds are generated which are called *Tombac*, *Dutch-gold*, and *Pinchbeck*. The *white copper* of the Chinese, which is the same as the German silver of the present day, is composed, according to the analysis of Fyfe, of 40·4 parts of copper, 25·4 of zinc, 31·6 of nickel, and 2·6 of iron.

The art of tinning copper consists in covering that metal with a thin layer of tin, in order to protect its surface from rusting. For this purpose, pieces of tin are placed upon a well-polished sheet of copper, which is heated sufficiently for fusing the tin. As soon as the tin liquefies, it is rubbed over the whole sheet of copper, and if the process is skilfully conducted, adheres uniformly to its surface. The oxidation of the tin, a circumstance which would entirely prevent the success of the operation, is avoided by employing fragments of resin or muriate of ammonia, and regulating the temperature with great care. The two metals do not actually combine; but the adhesion is certainly owing to their mutual affinity. —Iron, which has a weaker attraction than copper for tin, is tinned with more difficulty than that metal.

ALLOYS OF STEEL.

Messrs. Stodart and Faraday have succeeded in making some very important alloys of steel with other metals. (Phil. Trans. for 1822.) Their experiments induced them to believe that the celebrated Indian steel, called *wootz*, is an alloy of steel with small quantities of silicon and aluminium; and they succeeded in preparing a similar compound, possessed of all the properties of wootz. They ascertained that silver combines with steel, forming an alloy, which, although it contains only 1-500th of its weight of silver, is superior to wootz or the best cast steel in hardness. The alloy of steel with 100th part of platinum, though less hard than that with silver, possesses a greater degree of toughness, and is therefore highly valuable when tenacity as well as hardness is required. The alloy of steel with rhodium even exceeds the two former in hardness. The compound of steel with palladium, and of steel with iridium and osmium, is likewise exceedingly hard; but these alloys cannot be employed extensively, owing to the rarity of the metals of which they are composed.

ALLOYS OF SILVER.

Silver is capable of uniting with most other metals, and suffers greatly in malleability and ductility by their presence. It may contain a large quantity of copper without losing its white colour. The standard silver for coinage contains about 1-13th part of copper, which increases its hardness, and thus renders it more fit for coins and many other purposes.

ALLOYS OF GOLD.

The presence of other metals in gold has a remarkable effect in impairing its malleability and ductility. The metals which possess this property in the greatest degree are bismuth, lead, antimony, and arsenic. Thus, when gold is alloyed with 1-1920th part of its weight of lead, its malleability is surprisingly diminished. A very small proportion of copper has an influence over the colour of gold, communicating to it a red tint, which becomes deeper as the quantity of copper increases. Pure gold, being too soft for coinage and many purposes in the arts, is always alloyed either with copper or an alloy of copper and silver, which increases the hardness of the gold without materially affecting its colour or tenacity. Gold coins contain about 1-12th of copper.

Nearly all the gold found in nature is alloyed more or less with silver. In a late elaborate investigation into the constituents of the Uralian ores of gold, G. Rose found one specimen with 0·16 per cent. of silver, and another with 38·38 per cent.; but most of the specimens contained 8 or 9 per cent. of silver. It has been maintained that the native alloys of gold and silver are usually in atomic proportion. This statement, however, has been amply disproved by G. Rose: these metals appear to be isomorphous, and hence, like other isomorphous bodies, they crystallize with each other in proportions altogether indefinite. (Pog. An. xxiii. 161.)

SALTS.

GENERAL REMARKS ON SALTS.

The preceding pages contain the description either of elementary principles, or of compounds immediately resulting from the union of those elements. These compounds are chiefly bi-elementary, that is, arise from the union of two elements; their constituents are regarded, according to the electro-chemical theory, as possessing opposite electric energies, and as combined by virtue of such energies; and the names applied to them are partly constructed in reference to this theory. Thus in compounds of oxygen and chlorine, chlorine and iodine, sulphur and potassium, the term expressive of the genus or class of bodies to which each compound belongs, is derived from the electro-negative element; so that we do not say, chloride of oxygen, iodide of chlorine, and potassiuret of sulphur,—but, oxide of chlorine, chloride of iodine, and sulphuret of potassium; because oxygen has a higher electro-negative energy than chlorine, chlorine than iodine, and sulphur than potassium. The metals as a class are electro-positive to the non-metallic elements; but in relation to each other some of the metals are electro-positive, and others electro-negative. To the former belong those metals, the oxides of which are strong alkaline bases, such as potassium, sodium, and calcium; and among the latter are enumerated those, such as arsenic, antimony, and molybdenum, which are prone to form acids when they unite with oxygen.

Some of the bi-elementary compounds above referred to, though composed of very energetic elements, are themselves chemically indifferent, manifesting little disposition to unite with any other body whatever; of which the peroxides of manganese and lead, and some of the chlorides, are examples. Others, on the contrary, are surprisingly energetic in their chemical relations, and have an extensive range of affinity. The most remarkable instances of this are found among those oxidized bodies called *acids* and *alkalies*, the characters of which fixed the attention of chemists long before their composition was understood. The acids and alkalies, however, are indifferent to elementary substances: their affinities are exerted towards each other, and by uniting they give rise to compounds more complex than themselves, as containing at least three elements, and which are known by the name of *salts*. Acids and alkalies possess opposite electric energies in relation to each other, the former being − and the latter +. The electric energies evinced by them are related to the electric energies of their elements. Thus acids generally abound in the electro-negative oxygen, and if they contain a metal, it is usually an electro-negative metal; whereas the powerful alkalies are the protoxides of electro-positive metals.

Acids and alkalies neutralize each other more or less completely, so that the resulting salt is generally neither acid nor alkaline, and is far less energetic as a chemical agent than acids and alkalies. Most of them, however, unite in definite proportion with certain substances, such as water, alcohol, ammonia, and with other salts, forming the extensive family of *double salts*. To these compounds the electro-chemical theory may be extended: the two simple salts which constitute a double salt, may be viewed as two molecules united by virtue of electric energies of an opposite character.

In the early period of modern chemistry an acid was considered to be an oxidized body which has a sour taste, reddens litmus paper, and neutralizes alkalies. But subsequent experience has shown the propriety of extending the definition of an acid. For, first, the discovery of the hydracids proved that oxygen is not essential to acidity. Secondly, some compounds, owing to their insolubility, neither taste sour nor redden litmus, and yet from their chemical relations are regarded as acids. Thirdly, some acknowledged acids, such as the carbonic and hydrosulphuric, are unable fully to destroy the alkaline reaction of potassa. Facts of this kind have induced chemists to consider as acids all those compounds which unite with potassa or ammonia, and give rise to bodies similar in their constitution and general character to the salts which the sulphuric or some admitted acid forms with those alkalies.

A similar extension is given to the notion of alkalinity, the characters of which, as exhibited in their most perfect form in potassa and soda, are causticity, a peculiar pungent alkaline taste, alkaline reaction with test paper, and power both of neutralizing acids and of forming with them neutral saline compounds. Of these, chemists agree to consider the last as the most characteristic, and place among the *alkaline or salifiable bases* all those bodies which unite definitely with admitted acids, such as the sulphuric and nitric, and form with them compounds analogous in constitution to the salts which admitted alkalies form with the acids. Thus, magnesia is a very strong alkaline base, seeing that 20·7 parts of it neutralize as much sulphuric acid as 47 of potassa; and yet magnesia, from being insoluble, is all but tasteless, and has barely any alkaline reaction.

The progress of chemistry, which has gradually developed sounder views of the nature of acids and alkalies, is also causing an extension in the idea of a salt. The great mass of the salts are compounds of oxidized bodies, both the acid and the base containing oxygen. But ammonia, though not an oxide, has all the characters of alkalinity in an eminent degree, and its compounds with acids were at once admitted into the list of salts. Then came the discovery of the hydracids, such as the hydrochloric and hydriodic, which are so powerfully acid, that their compounds with alkaline bases were readily adopted as salts. Hence arose the division of the salts as a class into two orders, one containing the oxygen or oxy-salts, and the other the hydrogen or hydro-salts. Again, the gaseous terfluoride of boron, which contains neither oxygen nor hydrogen, combines definitely with ammonia, and forms with it a neutral compound, which was esteemed a salt as soon as it was known.

The notion of a salt has of late been still further extended. Chemists have long known that metallic sulphurets occasionally combine together, and constitute what is called a *double sulphuret.* In these compounds Berzelius, whose labours have greatly added to their number, has traced an exact analogy with the salts, and applied to them the name of *sulphur-salts.* The simple sulphurets by the union of which a sulphur-salt is formed, are bi-elementary compounds, strictly analogous in their constitution to acids and alkaline bases, and which, like them, are capable of assuming opposite electric energies in relation to each other. Electro-positive sulphurets, termed *sulphur bases*, are usually the protosulphurets of electro-positive metals, and therefore correspond to the alkaline bases of those metals; and the electro-negative sulphurets, *sulphur-acids*, are the sulphurets of electro-negative metals, and are proportional in composition to the acids which the same metals form with oxygen. Hence, if the sulphur of a sulphur-salt were replaced by an equivalent quantity of oxygen, an oxy-salt would result. (An. de Ch. et Ph. xxxii. 60.)

The compounds which Berzelius has enumerated as sulphur-acids, are the sulphurets of arsenic, antimony, tungsten, molybdenum, tellurium, tin, and gold. To these he has added the sulphurets of several other substances not metallic, such as sulphuret of selenium, bisulphuret of carbon, and the hydrosulphuric and hydrosulphocyanic acids. He mentions, also, that just as two electro-positive oxides may combine, one becoming electro-negative in regard to the other, so may a sulphur-salt be generated by the union of electro-positive sulphurets. The native double sulphuret of copper and iron, and a considerable number of similar compounds, are instances of this nature. These analogies are rendered much closer by the facts that hydrosulphuric and hydrosulphocyanic acids act as hydro-acids with ammonia, and as sulphur-acids with sulphur-bases; and that all the sulphurets which are remarkable as *sulphur-acids*, have likewise the property of combining with ammonia. —I shall accordingly place the double sulphurets as a third order of the class of salts, and describe them under the name of sulphur-salts.

A fourth order of salts has been formed by Berzelius, comprising for the most part bi-elementary compounds, which consist of a metal on the one hand, and of chlorine, iodine, bromine, fluorine, and the radicals of the hydracids on the other. He has applied to them the name of *haloid-salts* (from ἁλς sea-salt, and ειδος form), because in constitution they are analogous to sea-salt. The whole series of the metallic chlorides, iodides, bromides, and fluorides, such as chloride of sodium, iodide of potassium, and fluor-spar, as well as the cyanurets, sulphocyanurets, and ferrocyanurets, are included in his list of haloid-salts. (An. de Ch. et Ph. xxxii. 60.) The reader will at once perceive that these haloid-salts, as bi-elementary compounds, differ in composition from other salts, and are analogous to oxides and sulphurets.

The preceding pages contain an account of the different classes of compounds which have been termed salts. But since the last edition of this work was published, new views on this important class of bodies have begun to prevail. The researches of Graham on the phosphates, those of Liebig on the constitution of the organic acids and their salts, and the experiments of Dumas, Clark, Frémy, Thaulow, Péligot, and many others, have gradually converged to the point of recalling to the recollection of chemists certain profound views, first suggested by Davy in regard to chloric and iodic acids and their salts, and afterwards applied (apparently without previous knowledge of what Davy had done) by Dulong to the salts of oxalic acid. These views have the inestimable advantage of uniting all acids into one series, and all salts into another; nay, these two series may even be considered as one. I shall here briefly explain them; but in describing the salts individually, I shall retain the usual views of the constitution of acids and salts, as the former have been thus described in the preceding part of this volume, and the chemical world is not yet ripe for a complete change in the theory of salts. The new views, however, are making such rapid progress, and are so closely entwined with the details of every part of chemistry, that a knowledge of them is indispensable to the student.

In regard to acids, then, the first point to be noticed is, that all so-called oxygen acids, in the free, or what may be called the *active* state, contain hydrogen. On referring to the description of the mineral acids it will be found, for example, that they are described as combining with water when separated from their combinations. Oil of vitriol is SO_3,HO; nitric acid NO_5,HO, &c. The latter, indeed, cannot exist in the supposed anhydrous state, NO_5; and this is the case with a large majority of all known acids. Sulphuric acid and phosphoric acid, no doubt, may be obtained anhydrous, SO_3 and P_2O_5; but it is worthy of especial notice, that in this state *they do not possess the properties of these acids*, and only acquire them on the addition of water. The compound of dry sulphuric acid and ammonia, SO_3,NH_3, *is not* sulphate of ammonia, but a distinct compound. Moreover, these anhydrous acids combine with water with the greatest vehemence, and then assume their active characters. The principal exceptions are carbonic acid and chromic acid; but, on the other hand, none of the organic acids can exist without water, that is, without hydrogen.

It is obvious that hydrogen is essential to the hydracids. Now the view which I wish here to explain considers both these classes of acids as hydracids, and thus unites in one class or series bodies having the most perfect analogy in properties. According to this view, therefore, the general formula of a hydracid is $X + H$: X being an acid-radical which may be either simple or compound. Thus in hydrochloric, hydriodic, and hydrosulphuric acids respectively, X is represented by Cl,I, or S. In hydrocyanic and hydrosulphocyanic acids, X is represented by $Cy = C_2N$, and by $CyS_2 = C_2NS_2$, respectively.

In the hydrated oxygen acids of the preceding pages, to which alone, and not to the anhydrous acids, this theory applies, X is always a compound, and always contains oxygen. Thus in hydrated sulphuric acid, commonly so called, and represented by SO_3,

HO, X is represented by SO_4; in nitric acid, NO_5HO, $X = NO_6$; and in metaphosphoric acid, P_2O_5,HO, $X = P_2O_6$: and the true formulæ of these acids are SO_4,H,NO_6,H and P_2O_6,H, respectively.

Further, among the organic acids to be afterwards described, we find a corresponding constitution. In acetic acid (hydrated) $C_4H_3O_3,HO$, $X = C_4H_3O_4$; in hydrated formic acid, C_2HO_3, HO, $X = C_2HO_4$, &c.

The next point to be noticed is, that acids exist, the general formula of which is $X + H_n$; that is, in which X combines with two or more equivalents of H, and which are called polybasic acids. Those acids, above described, in which there is 1 eq. of H, are called monobasic acids. Where 2 eq. of H are present the acid is bibasic; with 3 eq. of H, tribasic, and so on. The reason of this nomenclature will appear when we come to salts.

Examples of this kind are, pyrophosphoric acid, $P_2O_5,2HO$, which is bibasic, its true formula being P_2O_7,H_2; phosphoric acid, $P_2O_5,3HO$, which is a tribasic acid, P_2O_8,H_3; and arsenic acid, $As_2O_5,3HO$; also a tribasic acid, As_2O_8,H_3.

But it is among the organic acids that we find the most numerous and striking examples of polybasic acids. The following table contains the formulæ of some of these.

Meconic acid	$C_{14}H\ O_{11}+3HO$(tribasic)$=C_{14}H\ O_{14}+H_3$.
Cyanuric acid	$Cy_3\ O_3+3HO$(tribasic)$=Cy_3\ O_6+H_3$.
Citric acid	$C_{12}H_5O_{11}+3HO$(tribasic)$=C_{12}H_5O_{14}+H_3$.
Tannic acid	$C_{18}H_5O_9+3HO$(tribasic)$=C_{18}H_5O_{12}+H_3$.
Tartaric acid	$C_8\ H_4O_{10}+2HO$(bibasic)$=C_8\ H_4O_{12}+H_2$.
Komenic acid	$C_{12}H_2O_8+2HO$(bibasic)$=C_{12}H_2O_{10}+H_2$.
Fulminic acid	$Cy_2\ O_2+2HO$(bibasic)$=Cy_2\ O_4+H_2$.
Mucic acid	$C_{12}H_8O_{14}+2HO$(bibasic)$=C_{12}H_8O_{16}+H_2$.

Moreover there are also polybasic acids which contain no oxygen, analogous in this respect to hydrochloric and hydrocyanic acids. Thus ferrocyanic acid is represented by $Cy_3Fe + H_2$; and ferridcyanic acid is $Cy_3Fe_2 + H_3$.

It will be obvious at a glance, that this theory of acids possesses the advantages of simplicity and of uniting in classification a vast number of bodies, similar in properties, which have formerly been arbitrarily separated. But the chief advantage attending it is, that it enables us to effect the same union into one class of all the salts of the acids containing hydrogen. It is in examining the salts, moreover, that we find the strongest arguments in favour of the theory as applied to acids.

A salt is formed, whenever one of these acids is neutralized by a metallic oxide, by ammonia, or by an organic base, or combines with them, without being neutralized.

Now, when a salt is thus formed, one phenomenon constantly occurs; this is the separation of *water*. In the simplest case, namely, where the hydracid of an elementary body acts on a metallic protoxide, the origin of the water is quite obvious. When hydrochloric acid, for example, acts on oxide of silver, chloride of silver is formed, and water is eliminated: $HCl + AgO = AgCl + HO$. There is here no doubt that the water is produced by the reaction.

But when hydrated sulphuric acid acts on the same oxide, although the phenomena are exactly the same, a different explanation is commonly given; and the water is assumed to have preexisted in the acid, thus, $SO_3,HO + AgO = SO_3,AgO + HO$.

It is contrary to all sound principles of reasoning to adopt two explanation of facts precisely similar; where one will suffice, and only one explanation of the former case is possible, we must apply the same explanation to the latter. This is done by the new theory; and the following formulæ will show the identity of the reaction in the two cases:—

$$H,Cl+Ag,O=Ag,Cl+H,O.$$
$$H,SO_4+AgO=Ag,SO_4+HO.$$

In both cases the water is formed by the union of the hydrogen of the acid with the oxygen of the oxide; and consequently in both cases the hydrogen of the acid has been replaced by the metal.

Here, then, is the theory of salts. A salt is formed when the hydrogen of the acid is replaced by its equivalent of a metal. Consequently, acids may be viewed as the hydrogen salts of their radicals, and thus acids and salts, in regard to their constitution, will form but one class.

As the metals replace hydrogen equivalent for equivalent, it is obvious that polybasic acids will form polybasic salts. This has already been illustrated under phosphoric acid, but other examples may be given. Thus, when cyanuric acid acts on oxide of silver, 3 atoms of the latter are required for one of the former, $(Cy_3O_6 + H_3) + 3AgO = (Cy_3O_6 + Ag_3) + 3HO$. With fulminic acid 2 atoms are required, $(Cy_2O_4 + H_2) + 2AgO = (Cy_2O_4 + Ag_2) + 2HO$. It is unnecessary here to multiply these examples.

One remarkable consequence, deducible from the theory under consideration is, that those oxides which most easily lose oxygen should most readily replace by their metal the hydrogen of the acid. This is found to be the case. For example, potash can only replace by potassium 2 of the 3 eq. of hydrogen in cyanuric acid, and 1 of the 2 eq. of hydrogen in fulminic acid, forming the compounds, $Cy_3O_6\begin{matrix}K_2\\H\end{matrix}\Big\{$ and $Cy_2O_4\begin{matrix}K\\H\end{matrix}\Big\}$ while with oxide of silver, an easily reducible oxide, the replacement as before mentioned, is complete. This fact furnishes an almost irresistible argument for the existence of hydrogen, as such, in acids; and further explains the formerly unaccountable fact, that the salts formed by the action of oxide of silver on organic acids are always anhydrous. In the case of phosphoric and arsenic acids also, oxide of silver forms anhydrous salts, or, in other words, replaces the hydrogen entirely, with much greater facility than potash or soda.

Another obvious consequence of this theory is, that the neutralizing power of an acid depends entirely on the number of equivalents of hydrogen replaceable by metals. Take, for example, hydrosulphuric acid, $S + H$; and add to the radical oxygen, &c., in almost any proportion, the neutralizing power remains unchanged, as the following table shows:—

	X=
Hydrosulphuric acid . . .	$S \quad +H.$
Sulphurous acid . . .	$SO_3 \ +H.$
Sulphuric acid . . .	$SO_4 \ +H.$
Hyposulphurous acid . .	$S_2O_3 \ +H.$
Hyposulphuric acid . .	$S_2O_6 \ +H.$
Hydrosulphocyanic acid . .	$S_2Cy \ +H.$
Chlorosulphuric acid . .	$SO_3Cl+H.$ (Regnault.)
Nitrosulphuric acid . .	$SNO_5+H.$ (Pelouze.)

No substances can be more different in composition than the above; yet they all neutralize exactly the same quantity of base; a fact readily explained, when it is considered that neutral salts result from the complete replacement of the hydrogen by metals.

The salts of ammonia form no exception to our theory. They always contain 1 at. of water, essential to their existence. Thus, sulphate of ammonia, anhydrous, contains $SO_3,NH_3,HO = SO_3,NH_4O = SO_4 + NH_4$. In this last formula, NH_4 represents the supposed metal ammonium, which, if it be a metal, only differs from ordinary metals in being compound, just as cyanogen, a compound acid radical, differs from chlorine.

I shall resume this subject when treating of the organic acids; and meantime I return to the description of the salts, according to the views still prevailing, with which the student must also make himself well acquainted, as they pervade all chemical works.

Consistently with the views developed in the first part of this section, I have grouped together all saline compounds which have a certain similarity of composition into one great class of *salts*, which is divided into the four following orders:—

Order I. The oxy-salts. This order includes no salt the acid or base of which is not an oxidized body.

Order II. The hydro-salts. This order includes no salt the acid or base of which does not contain hydrogen.

Order III. The sulphur-salts. This order includes no salt the electro-positive or negative ingredient of which is not a sulphuret.

Order IV. The haloid-salts. This order includes no salt the electro-positive or negative ingredient of which is not haloidal.

The nomenclature of the first order of salts was explained on a former occasion. The insufficiency of the division into *neutral*, *super*, and *sub*-salts will be made apparent by the following remarks. In the first place, some alkaline bases form more than one super-salt, in which case two or more different salts would be included under the same name. Secondly, some salts have an acid reaction, and might therefore be denominated super-salts, although they do not contain an excess of acid. Nitrate of oxide of lead, for instance, has the property of reddening litmus paper; whereas it consists of 1 eq. of oxide of lead and 1 eq. of nitric acid, and therefore in composition is precisely analogous to nitrate of potassa, which is a neutral salt. This fact was noticed some years ago by Berzelius, who accounted for the circumstance in the following manner:—The colour of litmus is naturally red, and it is only rendered blue by the colouring matter combining with an alkali. If an acid be added to the blue compound, the colouring matter is deprived of its alkali, and thus, being set free, resumes its red tint. Now on bringing litmus paper in contact with a salt, the acid and base of which have a weak attraction for each other, it is possible that the alkali contained in the litmus paper may have a stronger affinity for the acid of the salt than the base has with which it was combined; and in that case the alkali of the litmus being neutralized, its red colour will necessarily be restored. It is hence apparent that a salt may have an acid reaction without having an excess of acid.

The nomenclature of the hydro salts is framed on the same principles as that applied to the salts which contain oxygen. With respect to the third and fourth orders of salts no general principle of nomenclature has yet been agreed on. Berzelius has extended to them the same nomenclature which he employs for the oxy-salts, and some chemists seem disposed to follow his example; but as new views are apt to be obscured, and their intrinsic value overlooked, by being expressed in new language, I shall confine myself as much as possible to terms with which every chemist is familiar. It is worthy of consideration whether the nomenclature of the sulphur and haloid salts, instead of being purposely assimilated to that of the other salts, should not designedly be kept distinct, in order the more readily to distinguish between analogous compounds.

Nearly all salts are solid at common temperatures, and most of them are capable of crystallizing. The colour of salts is very variable, having no necessary connection with the colour of their elements. Salts composed of a colourless acid and base are colourless; but a salt, though formed of a coloured oxide or acid, may be colourless; or, if coloured, the tint may differ from that of both its constituents.

All soluble salts are more or less sapid, while those that are insoluble in water are insipid. Few salts are possessed of odour: the most remarkable one for this property is carbonate of ammonia.

Salts differ remarkably in their affinity for water. Thus some salts, such as the nitrates of lime and magnesia, are *deliquescent*, that is, attract moisture from the air, and become liquid. Others, which have a less powerful attraction for water, undergo no change when the air is dry, but become moist in a humid atmosphere; and others may be exposed without change to an atmosphere loaded with watery vapour.

Salts differ likewise in the degree of solubility in water. Some dissolve in less than their weight of water; while others require several hundred times their weight of this liquid for solution, and others are quite insoluble. This difference depends on two circumstances, namely, on their affinity for water, and on their cohesion; their solubility being in direct ratio with the first, and in inverse ratio with the second. One salt may have a greater affinity for water than another, and yet be less soluble; an effect which may be produced by the cohesive power of the salt which has the stronger attraction for water being greater than that of the salt which has a less powerful affinity for that liquid. The method proposed by Gay-Lussac for estimating the relative degrees of affinity of salts for water (An. de Ch. lxxxii.) is by dissolving equal quantities of salts in equal quantities of water, and applying heat to the solutions. That salt which has the greatest affinity for the menstruum will retain it with most force, and will therefore require the highest temperature for boiling.

Salts which are soluble in water crystallize more or less regularly when their solutions are evaporated. If the evaporation is rendered rapid by heat, the salt is usually deposited in a confused crystalline mass; but if it take place slowly, regular crystals are formed. The best mode of conducting the process is to dissolve a salt in hot water, and when it has become quite cold to pour the saturated solution into an evaporating basin, which is to be set aside for several days or weeks without being moved. As the water evaporates, the salt assumes the solid form; and the slower the evaporation, the more regular are the crystals. Some salts which are much more soluble in hot than in cold water, crystallize with considerable regularity when a boiling saturated solution is slowly cooled. The form which salts assume in crystallizing is constant under the same circumstances, and constitutes an excellent character by which they may be distinguished from one another.

Many salts during the act of crystallizing unite chemically with a definite portion of water, which forms an essential part of the crystal, but not of the salt, and is termed *water* of *crystallization.* The quantity of combined water is very variable in different saline bodies, but is uniform in the same salt. A salt may contain more than half its weight of water, and yet be quite dry. On exposing a salt of this kind to heat, it is dissolved, if soluble, in its own water of crystallization, undergoing what is termed the *watery fusion.* By a strong heat, the whole of the water is expelled; for no salt can retain its water of crystallization when heated to redness. Some salts, such as sulphate and phosphate of soda, lose a portion of their water, and crumble down into a white powder, by mere exposure to the air; a change which is called *efflorescence.* The tendency of salts to undergo this change depends on the dryness and coldness of the air; for a salt which effloresces rapidly in a moderately dry and warm atmosphere, may often be kept without change in one which is damp and cold.

The water of crystallization is retained by a very feeble affinity, as is proved by the phenomena of efflorescence, and by the facility with which such water is separated from the saline matter by a moderate heat, or by exposure to the vacuum of an air-pump at common temperatures. It is frequently observed, however, that a portion of the water is retained with such obstinacy that it cannot be expelled by a temperature short of that at which the salt is totally decomposed. This water, as in the case of the hydrated acids, is considered to act the part of a base, and is hence commonly called basic water, as has already been explained in the section on phosphorus. But from the observations of Graham it would appear that the water thus retained does not always act the part of a base, but is in a peculiar state of combination characteristically different both from basic water and water of crystallization (Ph. Tr. Ed. xii. 297). In his original paper he distinguished it as saline water; but in a recent report read to the meeting of the British Association in Liverpool, he has called it constitutional water. It is readily distinguished from water of crystallization, by being retained by a stronger affinity, and by being essential to the existence of the salt of which it constitutes a part. From basic water it differs by not being removed from its combinations even by the most powerful alkalines, whereas it is readily removed, and its place in the compound assumed by certain anhydrous salts: it is also expelled from an acid more readily than the basic water. From an example the character of water in these different states of combination will be readily understood. The crystals of the common phosphate of soda are composed of 1 eq. of phosphoric acid, 2 eq. of soda, and 25 eq. of water. On exposing them to a temperature of 212°, 24 eq. of the water are readily expelled; but the 25th eq. is retained with such power, that a red heat is necessary to effect its complete separation. By the loss of the 24 eq. of water, the crystalline form and texture of the salt is entirely destroyed, but the residual amorphous mass has all the properties of the common phosphate; whereas by the loss of the 25th, an entirely different salt, the pyrophosphate of soda, is produced. It will hence appear, that the 24 eq. of water which were lost at 212° were only essential to the existence of the crystal, while the loss of the 25th eq. affected that of the salt.

The same thing is observed in the case of sulphate of oxide of zinc. Its common crystals are composed of 1 eq. of sulphuric acid, 1 eq. of oxide of zinc, and 7 eq. of water, six of which are readily lost at 212°, the crystal being at the same time destroyed, while the 7th eq. is not expelled until the temperature rises above

410°. Thus far the 7th eq. of water in sulphate of zinc appears analogous to the 25th in the common phosphate of soda; but Graham has pointed out the remarkable difference that in the latter salt the eq. of water is readily removed from its combination by an eq. of any base which supplies its place in the compound; while in sulphate of zinc, the eq. of water is not affected by bases, but may be removed by anhydrous sulphates, which occupy its place and give rise to the formation of double salts. The former, as acting the part of a base, is called basic water; the latter, as influencing the constitution of a salt, is called constitutional water. The difference is denoted in symbols, by writing the basic water, as is the case with all bases, on the left side of the acid with which it is combined, and the constitutional water on the right. Hence the symb. of the crystals of phosphate of soda is $2NaO, HO. P_2O_5 + 24$ aq.; and of the sulphate of zinc, $ZnO\ SO_3\ HO + 6$ aq. In the phosphate the water may be removed by soda, forming $3NaO. P_2O_5 + 24$ aq.; in the sulphate, by anhydrous sulphate of potassa, forming the double salt $ZnO\ SO_3\ (KO\ SO_3)$.

In pursuing the study of this subject, Graham has been led to the conclusion that all salts are neutral in their constitution with the exception of certain classes. Thus he finds that the bisulphate of potassa is a double salt, formed by the constitutional water of sulphate of water being replaced by sulphate of potassa: thus

$$\begin{array}{c} HO\ SO_3HO \\ \&\ KO\ SO_3 \end{array} \ \text{yield}\ \begin{array}{c} HO\ SO_3\ (KO\ SO_3) \\ \&\ HO. \end{array}$$

To illustrate the constitution of a subsalt, the nitrates were selected. Nitric acid of sp. gr. 1·42 he considers to be nitrate of water with 3 eq. of constitutional water; its symb. is therefore $HO\ NO_5.\ 3HO$. But water corresponds with the class of isomorphous oxides of which magnesia, the oxides of zinc or of copper, may be taken as the type. Hence these oxides are capable of supplying the place of water in either state of combination, as is seen in the neutral and sub-nitrate of copper, in the former of which the basic water is replaced by an eq. of oxide of copper, while in the sub-salt the 3 eq. of constitutional water are replaced by 3 eq. of oxide of copper. Their constitution is therefore represented by the formulæ

$$KuO\ NO_5.\ 3HO.$$

$$\text{And } HO\ NO_5.\ 3Ku\,O.$$

In applying these views in other cases, however, difficulties arise, owing to the existence of anhydrous bisalts, as the anhydrous bisulphate and bichromate of potassa. These are accounted for by Graham, by supposing the existence of a class of bodies, called by him basic adjuncts, which admit of being attached to the oxide of hydrogen, or to the oxides of metals — the only true bases. The arguments in support of this view are principally drawn from the composition of the ammoniacal salts: it must be remembered, however, that the whole subject is in many respects hypothetical, and has not yet been sufficiently tested by experiment.

Salts, in crystallizing, frequently enclose mechanically within their texture particles of water, by the expansion of which, when heated, the salt is burst with a crackling noise into smaller fragments. This phenomenon is known by the name of *decrepitation.* Berzelius has correctly remarked that those crystals decrepitate most powerfully, such as the nitrates of baryta and oxide of lead, which contain no water of crystallization.

The atmospheric pressure is said to have considerable influence on the crystallization of salts. If, for example, a concentrated solution, composed of about three parts of sulphate of soda in crystals, and two of water, is made to boil briskly, and the flask which contains it is then tightly corked, while its upper part is full of vapour, the solution will cool down to the temperature of the air without crystallizing, and may in that state be preserved for months without change. Before removal of the cork, the liquid may often be briskly agitated without losing its fluidity; but on readmitting the air, crystallization commonly commences, and the whole becomes solid in the course of a few seconds. The admission of the air sometimes, indeed, fails in causing the effect; but it may be produced with certainty by agitation or the introduction of a solid body. The theory of this phenomenon is not very apparent. Gay-Lussac has shown that it does not depend on atmospheric pressure (An. de Ch. vol. lxxxvii.); for he finds that the solution may be cooled in open vessels without becoming solid, provided its surface be covered with a film of oil; and I have frequently succeeded in the same experiment without the use of oil, by causing the air of the flask to communicate with the atmosphere by means of a moderately narrow tube. It appears from some experiments of Graham (Phil. Trans. Edin. 1828), that the influence of the air may be ascribed to its uniting chemically with water; for he has proved that gases which are more freely absorbed than atmospheric air, act more rapidly in producing crystallization. Indeed, the rapidity of crystallization, occasioned by the contact of gaseous matter, seems proportional to the degree of its affinity for water.

The same quantity of water may hold several different salts in solution, provided they do not mutually decompose each other. The solvent power of water with respect to one salt is, indeed, sometimes increased by the presence of another, owing to combination taking place between the two salts.

Most salts produce cold during the act of solution, especially when they are dissolved rapidly and in large quantity. The greatest reduction of temperature is occasioned by those which contain water of crystallization.

All the oxy-salts are decomposed by voltaic electricity, provided they are either moistened or in solution. The acid appears at the positive pole of the battery, and the oxide at its opposite extremity; or if the oxide is of easy reduction, the metal itself goes over to the negative side, and its oxygen accompanies the acid to the positive wire.

The hydro-salts, and doubtless also the sulphur and haloid-salts, are subject to a similar change; but the phenomena as respects the two last orders of salts have been little examined.

ON CRYSTALLIZATION.

The particles of liquid and gaseous bodies, during the formation of solids, sometimes cohere together in an indiscriminate manner, and give rise to irregular shapeless masses; but more frequently they attach themselves to each other in a certain order, so as to constitute solids possessed of a symmetrical form. The process by which such a body is produced is called *crystallization;* the solid itself is termed a *crystal;* and the science, the object of which is to study the form of crystals, is *crystallography.*

Most bodies crystallize under favourable circumstances. The condition by which the process is peculiarly favoured is the slow and gradual change of a fluid into a solid, the arrangement of the particles being at the same time undisturbed by motion. This is exemplified during the slow cooling of a fused mass of sulphur or bismuth, or the spontaneous evaporation of a saline solution; and the origin of the numerous crystals, which are found in the mineral kingdom, may be ascribed to the influence of the same cause.

All substances are limited in the number of their crystalline forms. Thus, calcareous spar crystallizes in rhombohedrons, fluor-spar in cubes, and quartz in six-sided pyramids; and these forms are so far peculiar to those substances, that fluor-spar never crystallizes in rhombohedrons or six-sided pyramids, nor calcareous spar or quartz in cubes. Crystalline form may therefore serve as a ground of distinction between different substances. It is accordingly employed by mineralogists for distinguishing one mineral species from another; and it is very serviceable to the chemist as affording a physical character for salts. On this account I have thought it would be useful before describing the individual salts, to introduce a few pages on crystallization; but from the great extent of the subject, which now constitutes a separate science, my remarks must necessarily be limited, and comprehend little else than a brief outline of its more important principles. To those who are desirous of more ample information, I may recommend the "Elements of Crystallography," by Gustav Rose, or Mr. Whewell's Essay in the Phil. Trans. of London for 1825.

Every perfect crystal is bound by plane surfaces, which are called its faces. The straight line formed by the intersection of two faces is called an edge; the meeting of three or more edges in a point forms a solid angle. Thus in the octohedron, fig. 1, the bounding planes are the faces, the lines formed by their intersection the edges, the meeting of four of which in the same point produces a solid angle of the crystal.

The forms of crystals are exceedingly diversified. They are divided by crystallographers into simple and compound: a simple form has all its faces equal and similar to each other, while a compound form is bounded by at least two different classes of faces. Thus. figs. 1, 2, and 3, are simple forms; for the first is bounded by eight faces, each of which is an equilateral triangle, the second by six squares, and the third by twelve equal and similar rhombi.

Fig. 1.

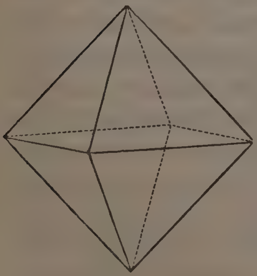


Fig. 2.

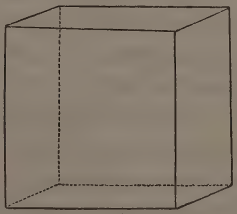
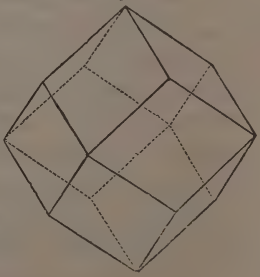


Fig. 3.



The forms represented by 4, 5, and 6, are, on the contrary, compound crystals: for fig. 4. is composed of two classes of faces, eight which are hexagonal, and six square; while fig. 6 contains three classes, eight faces being hexagonal, six octagonal, and twelve quadratic. This division into compound and simple is not artificial, but is founded on the fact that the compound forms are really produced by the combination of two or more of the simple crystals, as will be seen by a careful inspection of the forms and relative situations of the faces in the accompanying figures. The character of the faces in figures 1, 2, and 3, which represent respectively the regular octohedron, the cube, and the rhombic dodecahedron, is too obvious to demand comment; but to obtain a correct idea of the relative positions of the faces in these three forms requires a more careful investigation.

Fig. 4.

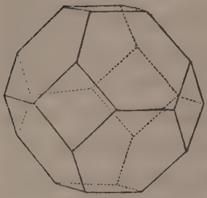


Fig. 5.

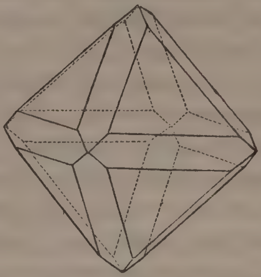
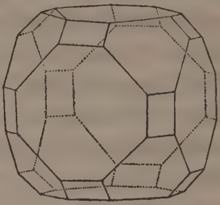


Fig. 6.



It will be observed that in each of these figures three right lines, which are equal in length, perpendicular to each other, and pass through the centre of the crystal, may be obtained;—in the octohedron by joining the opposite angles, in the cube by joining the centres of the opposite faces, and in the rhombic dodecahedron by connecting the opposite angles formed by the meeting of four edges, these angles being six in number and corresponding in situation to the six angles of the octohedron. The lines around which the different parts of the crystals are thus symmetrically grouped are called crystalline axes. Hence the above forms are connected by being possessed of the same axes of crystallization, and proceeding from these three equal and rectangular axes, either the octohedron, the cube, or the rhombic dodecahedron may be constructed, the resulting form being solely dependent on the law in accordance with which planes are symmetrically arranged or grouped around the axes. The octohedron (fig. 1) results from the law that every plane shall pass through an extremity of each axis: it will be evident that one, and only one, plane, fulfilling the required condition, may be introduced into each of the eight octants formed by the intersection of the three axes. This law, therefore, limits the number of faces to eight; and as these intersect each other in the lines joining the extremities of the axes, each face is an equilateral triangle, and the resulting form is the regular octohedron. The cube (fig. 2) results from the law that each plane shall pass through an extremity of one axis, and be parallel to the other two: as each of the three axes has two extremities, six, and only six, planes can be grouped around them in accordance with this law, and by their intersection the hexahedon, or cube, as it is more commonly called, is produced. In a similar manner may the rhombic dodecahedron (fig. 3) be shown to be formed according to the law that each plane shall pass through the extremities of two axes, and be parallel to the third.

The groups of simple forms, which are thus associated by being reducible from the same axes, constitute what is called by crystallographers a system of crystallization. Thus the octohedon, the cube, and the rhombic dodecahedron, are three forms of what is called the octohedral or regular system. Such forms are associated not merely by the similarity of their axis, but are connected still more intimately by the remarkable fact, that any substance which in crystallizing assumes one form of a system, may, and frequently does, assume other forms belonging to that system. Examples of this may be seen in the well-known salt alum, and in the black oxide of iron, the magnetic ore of mineralogists; the former generally crystallizing in the octohedron (fig. 1), but it may also be obtained in the form of the cube (fig. 2); and the magnetic iron ore is found not only in the form of octohedrons and cubes, but likewise in that of the rhombic dodecahedron (fig. 3). But, what is still more remarkable, the same substance is not only capable of assuming different forms of the same system, but during the act of crystallization the faces of two, three, four, and in some cases even more, of these forms are simultaneously developed, whereby compound crystals of the greatest diversity of form and appearance are produced. Thus, in the crystallization of alum either the cube or octohedron may be formed, but it is by far more common that the faces of both be produced, giving rise to the compound crystal represented in fig. 4, where the faces of the cube appear truncating the angles of the octohedron. Another form frequently observed in alum is represented by fig. 5, where in addition to the octohedron the faces of the rhombic dodecahedron are also developed; and as these are twelve in number, and correspond in situation to the twelve edges of the octohedron, their developement removes, or as it is technically expressed, truncates the twelve edges of the latter form. Fig. 6 represents a combination of all three forms. Similar and still more complicated combinations are observed on magnetic iron ore.

The importance of a knowledge of all the simple forms of a system, as being those in which the same substance may occur, and which alone can give rise to compound crystals, for simple forms of different systems are never combined, will be felt from what has already been stated. The first person who proved the existence of a mathematical connection between them was the celebrated crystallographer Haüy; but it is to Weiss, Professor of Mineralogy in Berlin, that we are indebted for the distinction of the system of crystallization,—a discovery which justly entitles him to the honour of being the founder of modern crystallography. He has shown that all crystalline forms may be brought under one of the six following systems, which may be conveniently distinguished as,

1. The octohedral, or regular system of crystallization.
2. The square prismatic ditto ditto.
3. The right prismatic ditto ditto.
4. The oblique ditto ditto.
5. The doubly oblique ditto ditto.
6. The rhombohedral system ditto ditto.

The Octohedral System.—This system is characterized by the three equal and rectangular axes, which have already been described. Let them be distinguished as the axes *a*, *b*, and *c*; and, for the convenience of reference, let us consider that the figure be brought into such a position that two of them, *a* and *b*, be horizontal, and *c* vertical. The figs. 1, 2, and 3 are drawn under this supposition. The law of crystalline symmetry is such, that if a face of a crystal be observed to bear a certain relation to one of the axes *a*, other faces must fulfil the same condition to the equal axes *b* and *c*. Thus, if a plane be seen to pass through the extremity of *a*, or be parallel to it, other planes must pass through the extremity of *b* and *c*, or be parallel to them. Owing to the perfect symmetry in the different parts of the crystal, this group is frequently called the regular system of crystallization.

It consists of but few simple forms, the number being necessarily limited to the number of different ways in which a plane can intersect the three axes. These, it will be seen, are only seven :—

1. The plane may cut each at an equal distance from the centre. The crystal the faces of which obey this law is the octohedron, fig. 1.

2. The plane may cut two axes at an equal, and the third at a greater distance from the centre. The resulting form is called the triakisoctohedron.

3. The plane may cut two axes at an equal, and the third at a less distance from the centre. The resulting form is the ikositetrahedron.

4. The plane may cut all three axes unequally. The form is the herakisoctohedron.

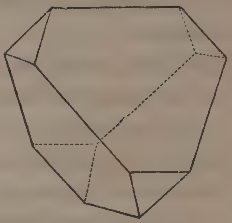
5. The plane may cut two axes at unequal distances from the centre, and be parallel to the third. The resulting crystal is the tetrakishexahedron.

6. The plane may cut two axes in points equally distant from the centre, and be parallel to the third. The form is the rhombic dodecahedron, fig. 3.

7. The plane may cut one axis, and be parallel to the other two. This law gives rise to the cube or hexahedron, fig. 2.

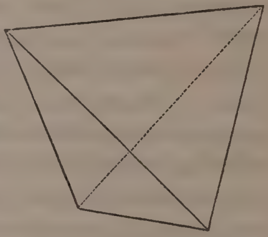
Of these forms, 1, 6, and 7 are of frequent occurrence; but the others are usually found only in combination, when their faces are generally small, and appear symmetrically arranged around the angles and on the edges of the former. Hence, in most compound crystals of this system, the faces either of the octohedron cube or rhombic dodecahedron may be readily recognized; and as these suffice to fix the position of the crystalline axes, they serve as a guide to determine the forms of the combination. Their prevalence presents also a remarkable instance of the tendence to simplicity which may be observed in all the processes of nature. This is not only seen in the greater simplicity of exterior form, but in the more definite nature of the laws by which the faces of these three crystals are determined; for while a plane has but one position in which it can satisfy the laws 1, 6, and 7, an unlimited number of planes may be found to satisfy the conditions expressed by 2, 3, 4, and 5. Thus, for example, there is but one way in which a plane can satisfy the law 1; while there are as many ways of satisfying the law 4, as there are of taking three lines which shall be unequal. Hence it follows that there can be but one octohedron, while the number of herakisoctohedrons is unlimited, and the faces of two different ones have been observed on the same crystals. The latter observation also applies to the forms produced according to the laws 2, 3, and 5; but the number of varieties which have been observed is very limited, and the relative lengths of the unequal axes may be expressed, almost without an exception, by the numbers 1, $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$, and $\frac{1}{5}$.

Fig. 7.



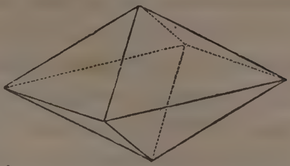
It is frequently observed in crystals of this system, that one-half of the faces of the crystals are much more developed than the other. This may be seen in figure 7, a crystal of the red oxide of copper, where four out of the eight faces of the octohedron have increased, and the other four proportionally diminished. The faces which increase, as well as those which diminish, always form two similar and symmetrically arranged groups, the increasing faces or groups of faces touching each other at the angular points of the crystal. Thus, in the octohedron, the four alternating faces which do not intersect in edges, but merely touch each other in the angular points, increase, as represented in figure 7, and by increasing till they form a perfect figure, give rise to the well known crystal the tetrahedron, fig. 8. These forms are called hemiedral, as denoting their origin: hence the tetrahedron is commonly known as the hemi-octohedron. Each of the simple forms of this system, with the exception of the cube and rhombic dodecahedron, gives rise to hemihedral crystals: the exception evidently results from the impossibility of dividing the faces of the cube and rhombic dodecahedron into two groups, which fulfil the necessary conditions.

Fig. 8.



The Square Prismatic System.—The forms of this system are, like those of the preceding, characterized by three axes, which intersect each other at right angles; but they differ from them by two only out of the three being equal. Let the third, which may be either greater or less than the two equal axes be called *c*, and let it be placed in a vertical position. The octohedron formed by joining the extremities of these axes, is either longer or shorter in the direction of the axis *c* than in that of its horizontal axes, as is

Fig. 9.



seen in fig. 9. From this it follows that these octohedrons may be compared to a double four-sided pyramid constructed on either side of a square base. The parts of the crystal about this base are therefore similar to each other, but differ from those about its upper or lower extremity; and as this observation applies equally to all forms of this system, it is the character by which the system is best distinguished. This difference is owing to the inequality of the vertical axis, which causes the relations of the faces to it to be unconnected with those they bear to the two horizontal axes. Hence it is common to find the lateral edges truncated without those connected with the extremities of the crystal being affected, whereby a square prism terminated by four-sided pyramids, as represented in fig. 10, is produced. The same may occur on the lateral angles as well as edges, as in fig. 11. In other cases, the terminal edges and angles are modified, but always in a different manner from the lateral.

Fig. 10.

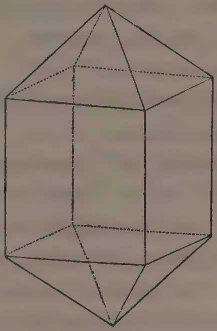
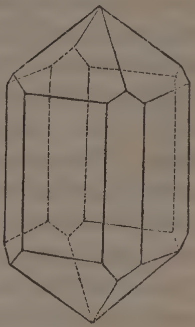


Fig. 11.



The Right Prismatic System.—The crystals of this system are, like the preceding, characterized by three rectangular axes, and are distinguished from both by no two of these axes being equal. Its forms are therefore not only distinguished by a difference in the lateral and terminal parts, but are still further marked by the difference between the front and back of the crystal, as compared with its sides. Thus in figs. 12, 13,

Fig. 12.

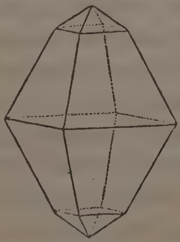


Fig. 13.

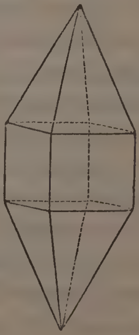
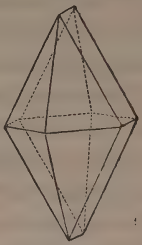
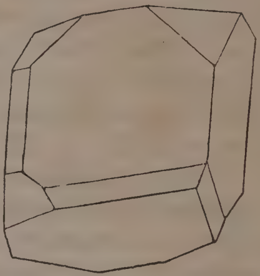


Fig. 14.



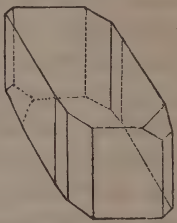
and 14, which represent three of the common forms of sulphur, the different magnitude in the parts of the crystals about each axis is perceptible, and sufficiently marks the different crystalline values of the three axes. But this is still better pointed out by the three different and independent modifications of the rhombic octohedron, which forms the basis of all three crystals.

Fig. 15.



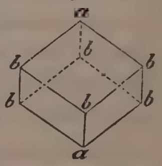
The Oblique Prismatic System.—The crystals of this system, of which an example may be seen in sulphate of the protoxide of iron, fig. 15, differ from those of the right prismatic system by the front and back parts being dissimilar. This difference is owing to two of the axes intersecting each other obliquely, while the third still remains perpendicular to both.

Fig. 16.



The Doubly Oblique System.—This system is readily recognized by the complete absence of all symmetry in its crystalline forms. This results from all three axes intersecting each other obliquely; owing to which the left and right sides, as well as the back and front, are of different crystalline values. From this it follows that no two faces are connected except those which are parallel, and all symmetry of form disappears, as observed in fig. 16, which represents a crystal of the sulphate of the oxide of copper.

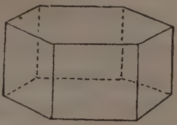
Fig. 17.



The Rhombohedral System.—The forms of this system of crystallization are, like the octohedral, characterized by three equal and similar axes; but these axes intersect each other at equal, but not at right angles. Its most simple form is the rhombohedron, fig. 17, which is bound by six equal and similar rhombic faces. The axes are obtained by joining the centre of the opposite faces. Although the faces of the rhombohedron are equal, two only of its angles, marked *a*, are regular, being formed by the meeting of three equal edges, while the other six are irregular. The line joining *a a* is called the principal axis of the rhombohedron, the angles *a* the terminal, and *b* the lateral angles of the rhombohedron.

The form which most commonly occurs associated with the rhombohedron is a hexagonal prism, fig. 18, two of which are observed, the one truncating the six angles, the other the lines joining these angles, the faces of the prism being in both cases parallel to the rhombohedral axes *aa*. The terminal angles *a* are frequently truncated by terminal planes.

Fig. 18.



The different forms of the system may be advantageously studied on crystals of quartz and calcareous spar.

Besides the distinction arising from external form, minerals are further distinguished by differences in the mechanical connection of their particles, peculiarities which mineralogists designate by the name of *structure*. The structure of a mineral arises from its particles adhering at some parts less tenaciously than at others, and consequently yielding to force in one direction more readily than in another. Structure is sometimes visible by holding a mineral between the eye and the light; but in general it is brought into view by effecting the actual separation of parts by mechanical means.

The structure of minerals may be *regular* or *irregular*. It is regular when the separation takes place in such a manner, that the detached surfaces are smooth and even like the planes of a crystal; and it is irregular, when the new surface does not possess this character.

A mineral which possesses a regular structure is said to be *cleavable*, or to admit of *cleavage;* the surfaces exposed by splitting or *cleaving* a mineral are termed the *faces of cleavage;* and the direction in which it may be cleaved is called the *direction of cleavage.* Sometimes a mineral is cleavable only in one direction, and is then said to have a *single* cleavage. Others may be cleaved in two, three, four, or more directions, and are said to have a *double*, *treble*, *fourfold* cleavage, and so on, according to their number.

Minerals that are cleavable in more than two directions may, by the removal of layers parallel to the planes of their cleavage, be often made to assume regular forms, though they may originally have possessed a different figure. Calcareous spar, for example, occurs in rhombohedrons of different kinds, in hexagonal prisms, in six-sided pyramids, and in various combinations of these forms;

but it has three sets of cleavage, which are so inclined to each other as to constitute a rhombohedron of invariable dimensions, and into that form every crystal of calcareous spar may be reduced. Lead glance possesses a treble cleavage, the planes of which are at right angles to each other; and hence it is always convertible by cleavage into the cube. The cleavages of fluor-spar are fourfold, and in a direction parallel to the planes of the regular octohedron, into which form every cube of fluor-spar may be converted.

Since the forms enumerated as belonging to the octohedral system of crystallization are possessed of fixed invariable dimensions, it is obvious that minerals, or other crystallized bodies included in that system, must often in their primary forms be identical with each other. In the other systems of crystallization this identity is not necessary, because the dimensions of their forms are variable. Thus octohedrons with a square base may be distinguished by the relative length of their axis, some being flat and others acute. Rhombic octohedrons may be distinguished from each other by the relative length of their axis, and the angles of their base. By Haüy it was regarded as an axiom in crystallography, that minerals not belonging to the octohedral system are characterized by their form; that though two minerals may in form be analogous, each for instance being a rhombic prism, the dimensions of those prisms are different. Identity of form in crystals not included in the octohedral system was thought to indicate identity of composition. But in the year 1819 a discovery, extremely important both to mineralogy and chemistry, was made by Mitscherlich of Berlin, relative to the connection between the crystalline form and composition of bodies. It appears from his researches,* that certain substances have the property of assuming the same crystalline form, and may be substituted for each other in combination without affecting the external character of the compound. Thus minerals having the crystallization and structure of garnet, and which from their appearance were believed to be such, have been found on analysis to contain different ingredients. Crystals possessed of the form and aspect of alum may be made with sulphates of potassa and peroxide of iron, without a particle of aluminous earth; and a crystal composed of selenic acid and soda will have a perfect resemblance to Glauber's salt. The axiom of Haüy, therefore, requires an essential modification.

To the new branch of science laid open by the discovery of

---

* Annales de Ch. et de Physique, vol. xiv. 172, xix. 350, and xxiv. 264 and 355.

Mitscherlich, the term *isomorphism* (from ισος equal, and μορφη form) is applied; and those substances which assume the same figure are said to be *isomorphous*. Of these isomorphous bodies several distinct groups have been described by Mitscherlich. One of the most instructive of these includes the salts of arsenic and phosphoric acid. Thus, the neutral phosphate and biphosphate of soda have exactly the same form as the arseniate and binarseniate of soda; phosphate and biphosphate of ammonia correspond to arseniate and binarseniate of ammonia; and the biphosphate and binarseniate of potassa have the same form. Each arseniate has a corresponding phosphate, possessed of the same form, possessing the same number of eq. of acid, alkali, and water of crystallization, and differing in fact in nothing, except that one series contains arsenic and the other an equivalent quantity of phosphorus. A second remarkable group contains the salts of sulphuric, selenic, chromic, and manganic acids. The salts of baryta, strontia, and oxide of lead constitute a third group; and a fourth consists of lime, magnesia, and the protoxides of manganese, iron, cobalt, nickel, zinc, and copper. A fifth includes alumina, peroxide of iron, and the green oxide of chromium; and a sixth group includes the salts of permanganic and perchloric acids. In comparing together isomorphous bodies of the same group, identity of form is not to be expected unless there is similarity of composition. A neutral phosphate does not correspond to a binarseniate, nor a biphosphate to a neutral arseniate; an anhydrous sulphate is not comparable to a hydrated seleniate of the same base; nor is sulphate of protoxide of iron, with 6 eq. of water, isomorphous with sulphate of protoxide of manganese with 5 eq. In all such instances, if chemical composition differ, crystalline form is also different.

The following table contains the principal groups of isomorphous substances at present observed by chemists: a more extended one, partly theoretical, has been drawn up by Professor Johnston, of Durham, in his Report on Chemistry to the British Association:—

1.	
Silver	Ag.
Gold	Au.
2.	
Arsenious Acid in its unusual form.	As_2O_3.
Sesquioxide of Antimony	Sb_2O_3.
3.	
Alumina	Al_2O_3.
Peroxide of Iron	Fe_2O_3.
4.	
Salts of	
Phosphoric Acid	P_2O_5.
Arsenic Acid	As_2O_5.
5.	
Salts of	
Sulphuric Acid	SO_3.
Selenic Acid	SeO_3.
Chromic Acid	CrO_3.
Manganic Acid	MnO_3.

Salts of	6.
Perchloric Acid	Cl_2O_7.
Permanganic Acid	Mn_2O_7.

Salts of	7.
Potassa	KO.
Ammonia with 1 eq. of water	H_4NO.

Salts of	8.
Soda	NaO.
Oxide of Silver	AgO.

Salts of	9.
Baryta	BaO.
Strontia	SrO.
Lime (in Arragonite)	CaO.
Protoxide of Lead	PbO.

Salts of	10.
Lime	CaO.
Magnesia	MgO.
Protoxide of Iron	FeO.
. . Manganese	MnO.
. . Zinc	ZnO.
. . Nickel	NiO.
. . Cobalt	CoO.
. . Copper	CuO.
. Lead in Plumbocalcite	PbO.

Salts of	11.
Alumina	Al_2O_3.
Peroxide of Iron	Fe_2O_3.
Oxide of Chromium	Cr_2O_3.
Sesquioxide of Manganese	Mn_2O_3.

The facts above mentioned afford indubitable proof that the form of crystals is materially dependent on their atomic constitution; and they at first induced Mitscherlich to suspect that crystalline form is determined solely by the number and arrangement of atoms, quite independently of their nature. Subsequent observation, however, induced him to abandon this view; and his opinion now appears to be, that certain elements, which are themselves isomorphous, when combined in the same manner with the same substance, communicate the same form. Similarly constituted salts of arsenic and phosphoric acids yield crystals of the same figure, because the acids, it is thought, are themselves isomorphous; and as the atomic constitution of these acids is similar, each containing the same number of atoms of oxygen united with the same number of atoms of the other ingredient, it is inferred that phosphorus is isomorphous with arsenic. In like manner it is believed that selenic acid must be isomorphous with sulphuric acid, and selenium with sulphur; and the same identity of form is ascribed to all those oxides above enumerated, the salts of which are isomorphous. The accuracy of this ingenious view has not yet been put to the test of extensive observation, because the crystalline forms of the substances in question are for the most part unknown. But our knowledge, so far as it goes, is favourable; for peroxide of iron and alumina, the salts of which possess the same form, are themselves isomorphous. It may hence be inferred as probable, that isomorphous compounds in general arise from isomorphous elements uniting in the same manner with the same substance.

Isomorphous substances have often very close points of resemblance, quite independently of form. Thus, arsenic and phosphorus have the same odour, they both form gaseous compounds with hydrogen, they differ from nearly all other bodies in their mode of combining with oxygen, and yet agree with one another, and their salts are disposed to combine with the same quantity of water of crystallization. A similar analogy subsists between selenium and sulphur, both being fusible, volatile, and combustible in nearly the same degree, forming with hydrogen colourless gases which are similar in odour and in their chemical relations, and giving rise to analogous compounds with oxygen. The characters of sulphuric and selenic acids in particular are very similar; and the salts of these acids are equally allied. Sulphate of soda, for example, has the unusual property of being less soluble in water at 212° than at 100°, and the very same peculiarity is observable in seleniate of soda. The same intimacy of relation exists between baryta and strontia, between lime and magnesia, and between cobalt and nickel.

Isomorphous substances, owing doubtless to the various points of resemblance which have just been traced, crystallize together with great readiness, and are separated from each other with difficulty. Daubeny has remarked that a weak solution of lime, which in pure water would be instantly indicated by oxalate of ammonia, is very sluggishly affected by that test when much sulphate of magnesia is present; and I find that chloride of manganese cannot be purified from lime by oxalate of ammonia. A mixture of the sulphates of the protoxides of copper and iron yields crystals which have the same quantity of water of crystallization (6 equivalents), and the same form, as green vitriol, though they may contain a large quantity of copper. The sulphates of the protoxides of zinc and copper, of copper and magnesium, of copper and nickel, of zinc and manganese, and of magnesium and manganese, crystallize together, contain 6 equivalents of water, and have the same form as green vitriol, without containing a particle of iron. These mixed salts may be crystallized over and over again without the ingredients being separated from each other, just as it is extremely difficult to purify alum from peroxide of iron, with which alumina is isomorphous. In these instances the isomorphous salts do not occur in definite proportions: they are not chemically united as double salts, but merely crystallize together.

The same intermixture of isomorphous substances which takes place in artificial salts is found to occur in minerals, and affords a luminous explanation of the great variety both in the kind and proportion of substances which may coexist in a mineral species, without its external character being thereby essentially affected. Thus, garnet is a double silicate of alumina and lime, expressed by the formula $(Al_2O_3 + SiO_3) + 3(CaO + SiO_3)$; but in garnet, as in alum, the alumina may be replaced by peroxide of iron, yielding the compound $(Fe_2O_3 + SiO_3) + (3CaO + SiO_3)$, or they may be both present in any proportion, provided that their sum is equivalent to either singly. So, while peroxide of iron displaces the alumina, the lime may be exchanged for protoxide of iron; and a mineral would result, $(Fe_2O_3 + SiO_3) + (3FeO + SiO_3)$, which contains neither alumina nor lime, though it has still the form of garnet. Instead of protoxide of iron, the lime may be replaced by magnesia, protoxide of manganese, or any other isomorphous base; or any equivalent quantity of some or all of these may take the place of the lime, without the crystallographic character being destroyed. In like manner epidote is a double silicate of alumina and lime, expressed by $(Al_2O_3 + SiO_3) + (CaO + SiO_3)$; and here again varieties of epidote are to be expected, in which alumina and lime are replaced partially or wholly by an equivalent quantity of isomorphous bases.

The discovery of Mitscherlich, while it accounts for difference of composition in the same mineral, and serves as a caution to mineralogists against too exclusive reliance on crystallographic character, is in several other respects of deep interest to the chemist. It tends to lay open new paths of research by unfolding analogies which would not otherwise have been perceived.—The tendency of isomorphous bodies to crystallize together accounts for the difficulty of purifying mixtures of isomorphous salts by crystallization.—The same property sets the chemist on his guard against the occurrence of isomorphous substances in crystallized minerals. The native phosphates, for example, frequently contain arsenic acid, and conversely the native arseniates phosphoric acid, without the form of the crystals being thereby affected in the slightest degree.—It is a useful guide in discovering the atomic constitution of compounds. All chemists are agreed, from the composition of the oxides of iron, and from the compounds which this metal forms with other bodies, that the peroxide consists of two atoms of iron and three atoms of oxygen; and therefore it is inferred that alumina, which is isomorphous with peroxide of iron, has a similar constitution. The green oxide and acid of chromium, the oxygen of which is as 1 to 2, afford a still better illustration. As the chromates and sulphates are isomorphous, it was inferred that chromic, like sulphuric, acid was composed of one atom of the combustible to three atoms of oxygen. On this presumption it follows that the green oxide, containing half as much oxygen as the acid, must contain two atoms of chromium to three atoms of oxygen; and agreeably to this inference it is found that the green oxide is isomorphous with alumina and peroxide of iron.—The phenomena presented by isomorphous bodies afford a powerful argument in favour of the atomic theory. The only mode of satisfactorily accounting for the striking identity of crystalline form observable, first, between two substances, and, secondly, between all their compounds which have an exactly similar composition, is by supposing them to consist of ultimate particles possessed of the same figure, and arranged in precisely the same order. Hence it appears, that, in accounting for the connection between form and composition, it is necessary to employ the very same theory, by which alone the laws of chemical union can be adequately explained.

It has been objected to some of the facts adduced in favour of isomorphism, that the forms of substances considered isomorphous are sometimes *approximate* rather than *identical*. The primary form of sulphate of strontia is a rhombic prism very similar to that of sulphate of baryta; but on measuring the inclination of corresponding sides in each prism, the difference is found to exceed two degrees; and similar differences are observable in the rhombohedron of the carbonates of lime and protoxide of iron. This has induced Professor Miller of Cambridge to indicate this *approximation* by the term *plesiomorphism* (πλησιος, near); and it has been brought forward in a clever essay by Brooke, as an argument against the whole doctrine of isomorphism, an essay which has received an able reply from the pen of Whewell. (Phil. Mag. and An. N. S. x. 161 and 401.)

In one of the essays above referred to, Mitscherlich observed that biphosphate of soda is capable of yielding two distinct kinds of crystals, which, though different in form, in composition appear to be identical. The more uncommon of the two forms resembled binarseniate of soda; but the more usual form is quite dissimilar. He has since discovered, that sulphur is capable of yielding two distinct kinds of crystals. The crystals of carbonate of lime in calcareous spar and in arragonite belong to different systems of crystallization, the former being rhombohedral, and the latter derived from a rhombic prism. Arsenious acid, and probably metallic arsenic also, affords an instance of the same kind. It would thus seem that elementary and compound bodies are capable of assuming two distinct crystalline forms. In the case of biphosphate of soda an explanation may be derived from the experiments of Graham on metaphosphoric acid; but the fact that an elementary substance is susceptible of assuming different forms is wholly unexplained.

Mitscherlich has also noticed that the form of salts is sometimes changed by heat, without their losing the solid state. This change was first noticed in sulphate of magnesia, and also in the sulphates of the protoxides of zinc and iron. It appears, in these instances at least, to be owing to decomposition of the hydrous salt effected by increased temperature; a change of composition which is accompanied with a new arrangement in the molecules of the compound.

SECTION I.

CLASS OF SALTS, ORDER I.

OXY-SALTS.

This order of salts includes no compound the acid or base of which does not contain oxygen. With the apparent exception of the ammoniacal salts, both the acid and base of the salts described in this section are oxidized bodies. As each acid, with few exceptions, is capable of uniting with every alkaline base, and frequently in two or more proportions, it is manifest that the salts must constitute a very numerous class of bodies. It is necessary, on this account to facilitate the study of them as much as posible by classification. They may be conveniently arranged by placing together those salts which contain either the same salifiable base or the same acid. It is not very material which principle of arrangement is adopted; but I give the preference to the latter, because, in describing the individual oxides, I have already mentioned the characteristic features of their salts, and have thus anticipated the chief advantage that arises from the former mode of classification. I shall therefore divide the salts into families, placing together those saline combinations which consist of the same acid united with different salifiable bases. The salts of each family, in consequence of containing the same acid, possess certain characters in common by which they may all be distinguished; and, indeed, the description of many salts, to which no particular interest is attached, is sufficiently comprehended in that of its family, and may therefore be omitted.

All the powerful alkaline bases, excepting ammonia, are the protoxides of an electro-positive metal, such as potassium, barium, or iron; so that if M represent an eq. of any one of those metals, $M + O$ or MO is the strongest alkaline base, and often the only one, which that metal can form. A single eq. of a monobasic acid neutralizes MO, forming with it a neutral salt. Thus, indicating an equivalent of sulphuric and nitric acid by the signs SO_3 and NO_5, all the neutral sulphates and nitrates of protoxides are indicated by $MO + SO_3$ and $MO + NO_5$. There is, therefore, in the neutral protosalts of each family, a constant ratio in the oxygen of the base and acid, resulting from the composition of each acid, that ratio for the sulphates being as 1 to 3, and for nitrates as 1 to 5. If the metal M of a neutral sulphate pass into a higher grade of oxidation, becoming a binoxide MO_2, then will that binoxide be disposed to unite with 2 eq. of acid, and form a bisalt, $MO_2 + 2SO_3$, in which the oxygen of base and acid is still as 1 to 3; and if the metal yield a sesquioxide, M_2O_3, then if sufficient acid be supplied, the resulting salt will consist of $M_2O_3 + 3SO_3$, the ratio of 1 to 3 being preserved. This curious law relative to oxy-salts, which is very general, was first noticed by Gay-Lussac (Mémoires d'Arcueil, ii.); and Berzelius has found it to hold in earthy minerals, and employed it as a guide in studying their composition.

The combination of salts with one another gives rise to compounds which were formerly called *triple* salts; but as the term *double* salt, proposed by Berzelius, gives a more correct idea of their nature and constitution, it will always be employed by preference. These salts may be composed of one acid and two bases, of two acids and one base, and of two different acids and two different bases. Most of the double salts hitherto examined consist of the same acid and two different bases.

The difference in the constitution of ammonia and that of all other bases capable of uniting with ox-acids, gives great interest to its salts. In another place, the probable existence of a compound radical formed of 1 eq. of nitrogen and 4 of hydrogen, and called by Berzelius ammonium, was pointed out. The oxide of this radical, which has not yet been obtained in an uncombined state, he considers as the basis of the oxy-salts of ammonia. This view is not supported by analogy alone, but is based on the remarkable fact, that in all the neutral salts of ammonia the quantity of water necessary to convert the ammonia into oxide of ammonium is always present, nor can it be removed without the total decomposition of the salt. H. Rose has indeed succeeded in obtaining anhydrous compounds of ammonia with the ox-acids; but he has at the same time shown that they cannot be considered as salts, for although containing the elements for forming an anhydrous and neutral salt of ammonia, and produced by direct combination, neither the acid nor the alkali is present in the compound. This he has proved particularly in the substance formed by the union of anhydrous sulphuric acid with ammonia (An. de Ch. et Ph. lxii. 389). Strong evidence in its favour is likewise obtained from the views of isomorphism. It has been proved by Mitscherlich that in all the crystallized salts of potassa, whether simple or double, the potassa may be replaced either partially or completely by an equivalent quantity of protohydrate of ammonia without any change in the form of the crystal. Ammonia with an eq. of water is therefore isomorphous with potassa. But all isomorphous substances, with this exception, have the same chemical constitution, and it is incompatible with the theory of isomorphism to suppose one alkali to be isomorphous with the hydrate of another. But that the oxide of a compound radical should be isomorphous with the oxide of a simple metal, is consistent with—nay, might be expected from, their known analogies.

Another view of the constitution of the oxy-salts of ammonia has recently been proposed by Graham. He supposes ammonia not to be a base, but to be one of a class of bodies which he calls basic adjuncts; a term used to denote a substance which, without being a base, is capable of entering into the constitution of a salt by attaching itself to other bases. Thus, the oxy-salts of ammonia he conceives to be salts of water, to the base of which ammonia is added as an adjunct. It is scarcely necessary to remark, that this view is not only inconsistent with the theory of isomorphism, but that the existence of adjunct bases is hypothetical, and arises from an endeavour to support another hypothesis, that all salts are neutral in composition.

SULPHATES.

The salts of sulphuric acid in solution may be detected by chloride of barium. A white precipitate, sulphate of baryta, invariably subsides, which is insoluble in acids and alkalies; a character by which the presence of sulphuric acid, whether free or combined, may always be recognized. An insoluble sulphate, such as sulphate of baryta or strontia, may be detected by mixing it, in fine powder, with three times its weight of carbonate of potassa or soda, and exposing the mixture in a platinum crucible for half an hour to a red heat. Double decomposition ensues; and on digesting the residue in water, filtering the solution, neutralizing the free alkali by pure hydrochloric, nitric, or acetic acid, and adding chloride of barium, the insoluble sulphate of that base is precipitated.

Several sulphates exist in nature, but the only ones which are abundant are the sulphates of lime and baryta. All of them may be formed by the action of sulphuric acid on the metals themselves, on the metallic oxides or their carbonates, or by way of double decomposition.

The solubility of the sulphates is very variable. There are six only which may be regarded as really insoluble; namely, the sulphate of baryta, and of the oxides of tin, antimony, bismuth, lead, and mercury. The sparingly soluble sulphates are those of strontia, lime, zirconia, yttria, and oxide of silver. All the others are soluble in water.

All the sulphates, those of potassa, soda, lithia, baryta, strontia, and lime excepted, are decomposed by a white heat. One part of the sulphuric acid of the decomposed sulphate escapes unchanged, and another portion is resolved into sulphurous acid and oxygen. Those which are easily decomposed by heat, such as sulphate of oxide of iron, yield the largest quantity of undecomposed sulphuric acid.

When a sulphate, mixed with carbonaceous matter, is ignited, the oxygen both of the acid and of the oxide unites with carbon, carbonic acid is disengaged, and a metallic sulphuret remains. A similar change is produced by hydrogen gas at a red heat, with formation of water, and frequently of some hydrosulphuric acid. In some instances the hydrogen entirely deprives the metal of its sulphur.

The composition of neutral protosulphates is expressed, as above stated, by the formula $MO + SO_3$. Consequently the acid contains three times as much oxygen as the base; and if both were deprived of their oxygen, a metallic protosulphuret would result, as indicated by the formula $M + S$.

In accordance with the views of Graham already given, the sulphates may be divided into three classes;—the first consisting of the anhydrous sulphates, being such as can exist without the eq. of constitutional water; the second, those in which the constitutional water forms an essential part; and the third composed of the double salts, which he considers as produced from the second by the eq. of constitutional water being replaced by an eq. of a sulphate of the first class. If dilute sulphuric acid be exposed in an open dish to a temperature not exceeding 380°, the evaporation proceeds without the slightest loss of acid until the sp. gr. is raised to 1·78, when it ceases entirely, and there remains a definite compound of 1 eq. of sulphuric acid and 2 eq. of water. One of these he considers as basic, the other as constitutional water, the acid of the mentioned strength being a salt the constitution of which is represented by the formula HO, SO_3, HO. From it any one of the three classes of sulphates may be formed, the eq. of basic water being readily replaced by any stronger base, while the eq. of constitutional water can only be removed by a neutral salt producing the double salts, among which the bisulphates must also be included. There are, however, exceptions to the last observation, as Graham has remarked that magnesia and its class of isomorphous oxides are capable of acting the part of constitutional water. Although it would be highly advantageous to treat of the sulphates under the three classes above mentioned, it cannot yet be attempted; for although the constitutional water of several of them has been determined by Graham in his valuable essay already quoted, many of them have not yet been examined in reference to this point. The following table represents the constitution of the more important, both in their amorphous and crystallized state:—

Names.	Base.	Acid.	Equiv.	Formulæ.
Sulphate of Potassa . .	47·15 1 eq.+	40·1 1 eq.=	87·25	$KO+SO_3$.
Sesquisulph. do. . .	94·3 2 eq.+	120·3 3 eq.=	214·6	$2KO+3SO_3$.
Do. in crystals with	9 or	1 eq. of water . .	=223·6	
Bisulph. Potassa . .	47·15 1 eq.+	80·2 2 eq.=	127·35	$KO+2SO_3$.
Do. with 9 or 1 eq. of water		. . . . .	=106·35	
Sulphate of Soda . .	31·3 1 eq.+	40·1 1 eq.=	71·4	$NaO+SO_3$.
Do. in crystals with	90 or	10 eq. of water . .	=161·4	
Bisulph. Soda . . .	31·3 1 eq.+	80·2 2 eq.=	111·5	$NaO+2SO_3$.
Do. in crystals with	36 or	4 eq. of water . .	=147·5	
Sulphate of Lithia . .	18 1 eq.+	40·1 1 eq.=	58·1	$LO+SO_3$.
Do. in crystals with	9 or	1 eq. of water . .	= 67·1	
Sulph. of ox. of Ammonium	26·15 1 eq.+	40·1 1 eq.=	66·25	H_4NO+3O_3.
Do. in crystals with	9 or	1 eq. of water . .	= 75·25	
Sulphate of Baryta . .	76·7 1 eq.+	40·1 1 eq.=	116·8	$BaO+SO_3$.
Do. Strontia .	51·8 1 eq.+	40·1 1 eq.=	91·9	$SrO+SO_3$.
Do. Lime . .	28·5 1 eq.+	40·1 1 eq.=	68·6	$CaO+SO_3$.
Do. as Gypsum with	18 or	2 eq. of water . .	= 86·6	

Names.	Base.		Acid.		Equiv.	Formulæ.
Sulphate of Magnesia	20·7	1 eq.+	40·1	1 eq.		
		+9 aq.	1 eq.		= 69·8	$MgO+SO_3HO$.
Do. in crystals with	54 or	6 eq. of water			=123·8	
Sulphate of Alumina	51·4	1 eq.+	40·1	1 eq.	= 91·5	$Al_2O_3+SO_3$.
Do. in crystals with	81 or	9 eq. of water			=172·5	
Tersulph. Alumina	51·4	1 eq.+	120·3	3 eq.	=171·7	$Al_2O_3+3SO_3$.
Do. in crystals with	162 or	18 eq. of water			=333·7	
Sulph. protox. Manganese	35·7	1 eq.+	40·1	1 eq.		
		+9 aq.	1 eq.		= 84·8	$MnO+SO_3HO$.
Do. in crystals with	36 or	4 eq. of water			=120·8	
Sulph. protox. Iron	36	1 eq.+	40·1	1 eq.		
		+9 aq.	1 eq.		= 85·1	$FeO+SO_3HO$.
Do. in crystals with	45 or	5 eq. of water			=130·1	
Tersulph. perox. Iron	80	1 eq.+	120·3	3 eq.	=210·3	$Fe_2O_3+3SO_3$.
Disulph. do.	160	2 eq.+	40·1	1 eq.	=200·1	$2FeO_3+SO_3$.
Do. as a hydrate with	54 or	6 eq. of water			=254·1	
Sulph. protox. Zinc	40·3	1 eq.+	40·1	1 eq.		
		+9 aq.	1 eq.		= 89·4	$ZnO+SO_3HO$.
Do. in crystals with	54 or	6 eq. of water			=143·4	
Sulp. protox. Nickel	37·5	1 eq.+	40·1	1 eq.		
		+9 aq.	1 eq.		= 86·6	$NiO+SO_3HO$.
Do. in crystals with	54 or	6 eq. of water			=140·6	
Sulp. protox. Cobalt	37·5	1 eq.+	40·1	1 eq.		
		+9 aq.	1 eq.		= 86·6	$CoO+SO_3HO$.
Do. in crystals with	49 or	5 eq. of water			=131·6	
Tersulph. ox. Chromium	80	1 eq.+	120·3	3 eq.	=200·3	$Cr_2O_3+3SO_3$.
Sulp. protox. Copper	39·6	1 eq.+	40·1	1 eq.		
		+9 aq.	1 eq.		= 88·7	$CuO+SO_3HO$.
Do. in crystals with	36 or	4 eq. of water			=124·7	
Disulphate do.	79·2	2 eq.+	40·1	1 eq.	=119·3	$2CuO+SO_3$.
Sulp. protox. Mercury	210	1 eq.+	40·1	1 eq.	=250·1	$HgO+SO_3$.
Subsulp. perox. do.	872	4 eq.+	120·3	3 eq.	=992·3	$4HgO_2+3SO_3$.
Bisulp. do.	218	1 eq.+	80·2	2 eq.	=298·2	HgO_2+2SO_3.
Sulp. ox. Silver	116	1 eq.+	40·1	1 eq.	=156·1	$AgO+SO_3$.

DOUBLE SULPHATES.

Sulphate of Soda and Lime	Sulphate of Soda	71·4	1 eq.	=140·0	NaO,SO_3+CaO,SO_3.
	do. Lime	68·6	1 eq.		
Sulp. of Potassa & Magnesia	Sulph. Potassa	87·25	1 eq.	=148·05	KO,SO_3+MgO,SO_3.
	do. Magnesia	60·8	1 eq.		
Do.	with 54 or 6 eq. of water			=202·05	
Sulp. ox. of Ammonium & Mag.	Sulph.ox.Ammonium	57·25	1 eq.	=127·05	H_4NO,SO_3+MgO,SO_3
	do. Magnesia	60·8	1 eq.		
Do.	with 54 or 6 eq. of water			=181·05	
Sulp. of Soda & Magnesia	Sulph. Soda	71·4	1 eq.	=132·2	NaO,SO_3+MgO,SO_3.
	do. Magnesia	60·8	1 eq.		
Do.	with 54 or 6 eq. of water			=186·2	
Sulp. of Potassa & Alumina	Sulph. Potassa	87·25	1 eq.	=258·95	$KO,SO_3;+Al_2O_33SO_3$.
	Tersulph. Alumina	171·7	1 eq.		
Do.	with 216 or 24 eq. of water			=474·95	

Sulph. of Soda & Alumina	Sulph. Soda	71·4	1 eq.	=243·1	$NaO,SO_3+Al_2O_3,3SO$
	Tersulph. Alumina	171·7	1 eq.		
Do.	with 234 or 26 eq. of water . . .			=477·1	
Sulph. ox. Am. & Alumina	Sulph.ox.Ammonium	57·25	1 eq.	=228·95	$H_4NO,SO_3+Al_2O_3,3S$
	Tersulph. Alumina	171·7	1 eq.		
Do.	with 216 or 24 eq. of water . . .			=444·95	
Sulph. Potassa & protox. Mang.	Sulph. Potassa	87·25	1 eq.	=163·05	KO,SO_3+MnO,SO_3.
	do. ox. Mangan.	75·8	1 eq.		
Do.	with 54 or 6 eq. of water . . .			=217·05	
Sulph.ox.Am.and protox. Mang.	Sulph. Ammonium	57·25	1 eq.	=133·05	H_4NO,SO_3+MnO,SO
	do. ox. Mang.	75·8	1 eq.		
Do.	with 54 or 6 eq. of water . . .			=196·05	

The protoxides of iron, zinc, nickel, and cobalt yield with potassa and ammonia double salts exactly agreeing in form and composition with the preceding double salts of magnesia and oxide of manganese.

Sulphate of Potassa.—This salt is easily prepared artificially by neutralizing carbonate of potassa with sulphuric acid; and it is procured abundantly by neutralizing with carbonate of potassa the residue of the operation for preparing nitric acid. Its taste is saline and bitter. It crystallizes in forms belonging to the right prismatic system, and its general form closely resembles the regular hexagonal prism, terminated by pyramids with six sides; the size of which is said to be much increased by the presence of a little carbonate of potassa. According to Mitscherlich it is isomorphous with chromate and seleniate of potassa. (Pog. Annalen, xviii. 168.) The crystals contain no water of crystallization, and suffer no change by exposure to the air. They decrepitate when heated, and enter into fusion at a red heat. They require 16 times their weight of water at 60°, and five of boiling water for solution.

Bisulphate of potassa is easily formed by exposing the neutral sulphate with half its weight of strong sulphuric acid to a heat just below redness, in a platinum crucible, until acid fumes cease to escape. It is obtained in crystals from a concentrated solution at high temperatures, as in the cold the neutral sulphates are formed. The form is a right rhombic prism, which is in general so flattened as to be tabular. According to Graham they contain 1 eq. of water, which he considers to be basic; the bisulphate being a double sulphate of water and potassa. The anhydrous bisulphate has been prepared by Rose. It has a strong sour taste, and reddens litmus paper. It is much more soluble than the neutral sulphate, requiring for solution only twice its weight of water at 60°, and less than an equal weight at 212° F. It is resolved by heat into sulphuric acid and the neutral sulphate.

Phillips has described a sesquisulphate, obtained in the form of acicular crystals like asbestos, from the residue of the process for making nitric acid. The conditions for insuring its production have not been determined. (Phil. Mag. and Annals, ii. 421.)

Sulphate of Soda.—This compound, commonly called *Glauber's salt*, is occasionally met with on the surface of the earth, and is frequently contained in mineral springs. It may be made by the direct action of sulphuric acid on carbonate of soda; and it is procured in large quantity as a residue in the processes for forming hydrochloric acid and chlorine.

Sulphate of soda has a cooling, saline, and bitter taste. It commonly yields forms belonging to the right prismatic system, and containing 10 eq. of water of crystallization, the whole of which is rapidly lost by efflorescence on exposure to the air. When heated they readily undergo the watery fusion. At 32°, 100 parts of water dissolve 12 parts of the crystals, 48 parts at 64·5°, 100 parts at 77°, 270 at 89·5°, and 322 at 91·5°. On increasing the heat beyond this point, a portion of the salt is deposited, being less soluble than at 91·5°. (Gay-Lussac.) If a solution saturated at 91·5° is evaporated at a higher temperature, the salt is deposited in opaque anhydrous prisms, unconnected, but of the same system as the hydrous crystals. Its sp. gr. in this state is 2·462. (Haidinger.)

Bisulphate of soda may be formed in the same manner as the analogous salt of potassa.

Sulphate of Lithia.—This salt is very soluble in water, fuses by heat more readily than the sulphates of the other alkalies, and crystallizes in flat prisms, which resemble sulphate of soda in appearance, but do not effloresce on exposure to the air. Its taste is saline without being bitter.

Sulphate of Oxide of Ammonium.—This salt is easily prepared by neutralizing carbonate of ox. of ammonium with dilute sulphuric acid; and it is contained in considerable quantity in the soot from coal. It crystallizes in long flattened six-sided prisms. It dissolves in two parts of water at 60°, and in an equal weight of boiling water. In a warm dry air it effloresces and loses 1 eq. of water. When sharply heated, it fuses, and is decomposed, yielding nitrogen gas, water, and sulphite of ox. of ammonium.

The anhydrous compound was formed by Rose by conducting dry ammoniacal gas into a glass vessel coated by a thin film of perfectly anhydrous sulphuric acid. When no excess of acid is present, it undergoes no change in the air, and is soluble without change in water, from which it crystallizes irregularly, but in forms different from those of the common sulphate. It is remarkable that the sulphuric acid is only partially precipitated by chloride of barium in the cold, and no precipitate whatever is produced by chlorides of strontium or lime until heat is applied, and even then the action is imperfect. Nor, on the other hand, can the ammonia be separated by the chloride of platinum. From this it follows that neither the sulphuric acid nor the ammonia can be present in the solution, although their elements are present in equivalent proportions. It is not improbable it may be an amide, and formed of $H_2NSO_2 + HO$.

Sulphate of Baryta.—Native sulphate of baryta, commonly called *heavy spar*, occurs abundantly, chiefly massive, but sometimes in anhydrous crystals, the form of which is variable, being sometimes prismatic and sometimes tabular, deducible from a right rhombic prism. Its density is about 4·4. It is easily formed artificially by double decomposition. This salt bears an intense heat without fusing or undergoing any other change, and is one of the most insoluble substances with which chemists are acquainted. It is sparingly dissolved by hot and concentrated sulphuric acid, but is precipitated by the addition of water.

Sulphate of Strontia.—This salt, the *celestine* of mineralogists. is less abundant than heavy spar. It occurs in anhydrous prismatic crystals of peculiar beauty in Sicily, and is isomorphous with the sulphate of baryta. Its density is 3·858. As obtained by the way of double decomposition, it is a white heavy powder, very similar to sulphate of baryta, and requires about 3840 times its weight of boiling water for solution.

Sulphate of Lime.—This salt is easily formed by mixing in solution a salt of lime with any soluble sulphate. It occurs abundantly as a natural production. The mineral called *anhydrite* is anhydrous sulphate of lime; and all the varieties of *gypsum* are composed of the same salts, united with water. The pure crystallized specimens of gypsum are sometimes called *selenite;* and the white compact variety is employed in statuary under the name of *alabaster*. The crystals of anhydrite belong to the right prismatic system, and are isomorphous with the sulphates of baryta and strontia, while the forms of gypsum are oblique prismatic. The latter, which are by far the more general, are readily recognized by the perfect cleavage plane which truncates the acute angle of the prism. They contain 2 eq. of water, one only of which is considered by Graham to be water of crystallization, the other being constitutional. The former is readily lost by exposing pounded gypsum to a temperature of 212° *in vacuo*, and the whole water is expelled by a temperature below 300°. Thus dried, it constitutes the well-known plaster of Paris, which, when mixed with a proper proportion of water, rapidly becomes dry and solid, owing to the eproduction of gypsum. It is remarkable, however, that gypsum which has lost only 1 eq. of water, as well as that which is dried by a heat exceeding 270°, will not act in a similar manner. In the latter case, the powder is a perfect anhydrite. (Phil. Mag. vi. 417.)

Sulphate of lime has hardly any taste. It is considerably more soluble than the sulphate of baryta or strontia, requiring for solution about 500 parts of cold, and 450 of boiling water. Owing to this circumstance, and to its existing so abundantly in the earth, it is frequently contained in spring water, to which it communicates the property called hardness. When freshly precipitated, it may be dissolved completely by dilute nitric acid. It is commonly believed to sustain a white heat without decomposition; but Thomson states that it parts with some of its acid when heated to redness.

Sulphate of Magnesia.—This sulphate, generally known by the name of *Epsom* salt, is frequently contained in mineral springs. It may be made directly, by neutralizing dilute sulphuric acid with carbonate of magnesia; but it is procured for the purposes of commerce by the action of dilute sulphuric acid on magnesian limestone, native carbonate of lime and magnesia.

Sulphate of magnesia has a saline, bitter, and nauseous taste. It crystallizes readily in small quadrangular prisms, which effloresce slightly in a dry air. It is obtained also in larger crystals, the principal form in which is a right rhombic prism, the angles of which are 90° 30′ and 89° 30′.—(Brooke.) Its crystals are soluble in an equal weight of water at 60°, and in three-fourths of their weight of boiling water. They undergo the watery fusion when heated; and the anhydrous salt is deprived of a portion of its acid at a white heat. Dried at 212° it retains 2 eq. of water; but one of these is expelled at 270°, while the other is retained till the temperature rises to 460°.

Sulphates of Alumina.—The tersulphate is prepared by saturating dilute sulphuric acid with hydrated alumina, and evaporating. It crystallizes with difficulty in thin flexible plates of a pearly lustre, which contain 18 eq. of water, and require twice their weight of water for solution. Berzelius says it occurs native at Milo in the Grecian Archipelago. It has an acid reaction.

The hydrated disulphate is known to mineralogists under the name of *aluminite*, which occurs at Halle, on the river Saal, and at Newhaven in Sussex; and Berzelius says the same compound falls when ammonia is added to a solution of the tersulphate. It is insoluble in water, and by heat is first rendered anhydrous, and then its acid is expelled, leaving pure alumina. The composition given in the table is from an analysis of aluminite from both its localities by Stromeyer.

Sulphate of Protoxide of Manganese.—This salt is best obtained by dissolving pure carbonate of manganese in moderately dilute sulphuric acid, and setting the solution aside to crystallize by spontaneous evaporation. The crystals are transparent, and of a slight rose tint, in taste resemble Glauber's salt, and belong to the doubly oblique prismatic system. It is insoluble in alcohol, but dissolves in twice and a half its weight of cold water. If the heat is gradually applied, it may be increased to redness without expelling any of the acid.

Sulphates of the Oxides of Iron.—Sulphate of the protoxide, commonly called *green vitriol*, is formed by the action of dilute sulphuric acid on metallic iron, or by exposing protosulphuret of iron in fragments to the combined agency of air and moisture. The salt has a strong styptic, inky taste. When perfectly pure it does not change vegetable blue colours, though generally stated to do so, the reddening effect being only produced when some of the iron passes into a higher state of oxidation, as has been shown by Bonsdorff (Pogg. An. xxxi. 81). He finds that the oxidation, which occurs with extreme facility in a perfectly neutral solution, is completely prevented by a few drops of sulphuric acid in excess, and the resulting crystals have a distinctly blue colour. The common green tint is consequently a delicate test of the presence of peroxide of iron. The crystals belong to the oblique prismatic system, and contain 6 eq. of water, one of which is retained, according to Graham, till the temperature rises to 535°. By operating carefully it may be rendered anhydrous without the loss of acid. It is soluble in two parts of cold and in three-fourths of its weight of boiling water. This salt is employed in the manufacture of fuming sulphuric acid.

The tersulphate of the peroxide is formed by mixing with a solution of the protosulphate exactly half as much sulphuric acid as that salt contains, and adding to the mixture in a boiling state successive portions of nitric acid until nitrous acid fumes cease to appear. The solution is then evaporated to dryness to expel the excess of nitric acid, and the tersulphate remains as a white salt. After being strongly heated, it dissolves slowly in water; but if evaporated at a gentle heat, it is deliquescent, and very soluble in water and alcohol, but insoluble in strong sulphuric acid. At a red heat it gives out all its acid, and peroxide of iron is left. Its solution in water has an orange colour, which is yellow when much diluted.

The disulphate of the peroxide falls as a hydrate of an ochreous colour, when a solution of the protosulphate is kept in an open vessel.

Sulphate of Oxide of Zinc.—This salt, frequently called *white vitriol*, is the residue of the process for forming hydrogen gas by the action of dilute sulphuric acid on metallic zinc; but it is also made, for the purposes of commerce, by roasting native sulphuret of zinc. It crystallizes by spontaneous evaporation in transparent flattened four-sided prisms of the right prismatic system, and isomorphous with Epsom salts. The crystals dissolve in two parts and a half of cold, and are still more soluble in boiling water. The taste of this salt is strongly styptic. It reddens vegetable blue colours, though in composition it is a strictly neutral salt.

Sulphate of Protoxide of Nickel.—This salt, like the salts of nickel in general, is of a green colour, and crystallizes from its solution in pure water in right rhombic prisms exactly similar to the sulphates of zinc and magnesia. If an excess of sulphuric acid is present, the crystals are square prisms, which, according to R. Phillips and Cooper, contain rather less water and more acid than the preceding; though the difference is not so great as to indicate a different atomic constitution. (Annals of Philosophy, xxii. 439.) Thomson says he analyzed both kinds, and found their composition identical. It is soluble in about three times its weight of water at 60° F.

Sulphate of Protoxide of Cobalt.—When protoxide of cobalt is digested in dilute sulphuric acid, a red solution is formed, which by evaporation deposits crystals of the same colour. Mitscherlich has shown that the crystals are identical in composition with sulphate of protoxide of iron; and Brooke's measurements prove these salts to be isomorphous. (An. of Phil. N. S. vi. 120.)

They are insoluble in alcohol, and dissolve in about 24 parts of cold water.

Tersulphate of Oxide of Chromium.—This salt may be formed by saturating dilute sulphuric acid with hydrated oxide of chromium; but it has not been obtained in crystals.

Sulphates of the Oxides of Copper.—Sulphate of the red oxide of copper has not been obtained in a separate state. The sulphate of the black, or protoxide, *blue vitriol*, employed by surgeons as an escharotic and astringent, may be prepared by roasting the native sulphuret; but it is more generally made by directly dissolving the protoxide in dilute sulphuric acid, and crystallizing by evaporation. This salt forms crystals of a blue colour, reddens litmus paper, and is soluble in about four of cold, and in two parts of boiling water. The crystals contain 5 eq. of water, four of which are lost at 212° in a dry air, but the fifth is retained till the temperature exceeds 430°. It is then a white powder, which combines readily with water, with the development of considerable heat. It is isomorphous with sulphate of protoxide of manganese.

When pure potassa is added to a solution of the sulphate of protoxide of copper in a quantity insufficient for separating the whole of the acid, a pale bluish-green precipitate, the disulphate, is thrown down.

Sulphate of protoxide of copper and ammonia is generated by dropping pure ammonia into a solution of the sulphate, until the sub-salt at first thrown down is nearly all dissolved. It forms a dark blue solution, from which, when concentrated, crystals are deposited by the addition of alcohol. It may be formed also by rubbing briskly in a mortar two parts of crystallized sulphate of protoxide of copper with three parts of carbonate of ammonia, until the mixture acquires an uniform deep blue colour. Carbonic acid gas is disengaged with effervescence during the operation, and the mass becomes moist, owing to the water of the blue vitriol being set free.

This compound, which is the *ammoniuret of copper* of the pharmacopœia, contains sulphuric acid, protoxide of copper, and ammonia; but its precise nature has not been determined in a satisfactory manner. It parts gradually with ammonia by exposure to the air.

Sulphates of the Oxides of Mercury.—When two parts of mercury are gently heated in three parts of strong sulphuric acid, so as to cause slow effervescence, a sulphate of the protoxide of mercury is generated. But if a strong heat is employed in such a manner as to excite brisk effervescence, and the mixture is brought to dryness, a bisulphate of the peroxide results, both being anhydrous. (Donovan in An. of Phil. xiv.) When this bisulphate, which is the salt employed in making corrosive sublimate, is thrown into hot water, decomposition ensues, and a yellow sub-salt, formerly called *turpeth mineral,* subsides. This salt is said by Phillips to consist of 3 eq. of acid and 4 of the peroxide. The hot water retains some of the bisulphate in solution, together with free sulphuric acid.

Sulphate of Oxide of Silver.— As this salt is rather sparingly soluble in water, it may be formed by double decomposition from concentrated solutions of nitrate of oxide of silver and sulphate of soda. It may also be procured by dissolving silver in sulphuric acid which contains about a tenth part of nitric acid, or by boiling silver in an equal weight of concentrated sulphuric acid. It requires about 80 times its weight of hot water for solution, and the greater part is deposited in small needles on cooling. By slow evaporation from a solution containing a little nitric acid, Mitscherlich obtained it in the form of a rhombic octohedron, the angles of which are almost identical with that of anhydrous sulphate of soda. Seleniate of oxide of silver is isomorphous with the sulphate.

Sulphate of oxide of silver forms with ammonia a double salt, which crystallizes in rectangular prisms, the solid angles and lateral edges of which are commonly replaced by tangent planes. It consists of 1 eq. of oxide of silver, 1 of acid, and 2 of ammonia; and it is formed by dissolving sulphate of oxide of silver in a hot concentrated solution of ammonia, from which on cooling the crystals are deposited. This salt is isomorphous with a double chromate and seleniate of oxide of silver and ammonia, which have a similar constitution, and are formed in the same manner. (Mitscherlich in An. de Ch. et Ph. xxxviii. 62.)

DOUBLE SULPHATES.

Sulphates of Lime and Soda.—This compound, the glauberite of mineralogists, occurs in very flat oblique rhombic prisms. Berthier prepared it by fusing together sulphate of lime with sulphate of soda in the ratio of their equivalents. Sulphate of soda fused in similar proportions with the sulphates of magnesia, baryta, and oxide of lead, gives analogous compounds. In these instances however, the affinity is so feeble, that it is overcome by the mere action of water. (An. de Ch. et Ph. xxxviii. 255.)

Sulphate of Potassa and Magnesia.—On mixing solutions of these salts in atomic proportion, the double salt is formed either by spontaneous evaporation or on cooling from a hot rather concentrated solution. The crystals are prismatic, and of a complicated form, belonging to the oblique prismatic system. (Brooke.) A similar double salt, isomorphous with the preceding, is formed by substituting ammonia for potassa. Their composition is given in the table.

Similar pairs of double salts may be formed with the protoxides of iron, zinc, cobalt, and nickel. These salts have the same form and composition as the corresponding salt of magnesia.

Alum.— This well-known substance is a double sulphate of potassa and alumina, which crystallizes with great facility from a solution containing its elements. It is prepared in this country from alum-slate, an argillaceous slaty rock highly charged with pyrites: on roasting this rock, the sulphuret of iron is oxidized, the resulting sulphuric acid unites with alumina and potassa present in the slate, and the alum is dissolved out by water. By frequent crystallization it is purified from the oxide of iron, which obstinately adheres to it. In Italy it is prepared from *alum-stone*, which occurs at Tolfa near Rome, and in most volcanic districts, being formed apparently by the action of sulphurous acid vapours on felspatic rocks. The materials of the alum exist in the stone ready formed; and they are extracted by gently heating the rock, exposing it for a time to the air, and lixiviation. The alum from this source has been long prized, in consequence of being quite free from iron. In both of these processes the alkali contained in the alum-rock is inadequate for uniting with the sulphate of alumina which is obtained, and hence a salt of potassa must be added.

Alum has a sweetish astringent taste, and reddens litmus paper. It is soluble in five parts of water at 60°, and in little more than its own weight of boiling water. It crystallizes readily in octohedrons, or in segments of the octohedron, and the crystals contain 24 eq. or almost 50 per cent. of water of crystallization. On being exposed to heat, they froth up remarkably, and part with all the water, forming anhydrous alum, the *alumen ustum* of the pharmacopœia. At a full red heat the alumina is deprived of its acid.

Alum is employed in the formation of a spontaneously inflammable mixture long known under the name of *Homberg's pyro-*

phorus. It is made by mixing equal weights of alum and brown sugar, and stirring the mass over the fire in an iron or other convenient vessel till quite dry: it is then put into a glass tube or bottle, and heated to moderate redness without exposure to the air, until inflammable gas ceases to be evolved. A more convenient mixture is made with three parts of lamp-black, four of burned alum, and eight of carbonate of potassa. When the pyrophorus is well made, it speedily becomes hot on exposure to the air, takes fire, and burns like tinder; but the experiment frequently fails from the difficulty of regulating the temperature.

From some recent experiments by Gay-Lussac, it appears that the essential ingredient of Homberg's pyrophorus is sulphuret of potassium in a state of minute division. The charcoal and alumina act only by being mechanically interposed between its particles; but when the mass once kindles, the charcoal takes fire and continues the combustion. He finds that an excellent pyrophorus is made by mixing 27 parts of sulphate of potassa with 15 parts of calcined lamp-black, and heating the mixture to redness in a common hessian crucible, of course excluding the air at the same time. (An. de Ch. et Ph. xxxvii. 415.)

Alum, having exactly the same form, composition, appearance, and taste, as the salt just described, may be made with ammonia, the sulphate of which replaces sulphate of potassa. It is met with occasionally as a natural product, and may be prepared by evaporating a solution of sulphate of ammonia with tersulphate of alumina.

A soda alum may also be prepared, similar in form and composition to the preceding alums, except that it contains 26 equivalents of water. (Berzelius.) This salt is disposed to effloresce in the air.

Iron Alum.—By mixing sulphate of potassa with tersulphate of peroxide of iron, and crystallizing by spontaneous evaporation, crystals are obtained similar to common alum in form, *colour*, *taste*, and composition. This salt has often a pink tint, but is sometimes quite colourless. A similar double salt, quite colourless, may be made with ammonia instead of potassa. In both these alums the alumina is simply replaced by an equivalent quantity of peroxide of iron.

Chrome Alums.—The tersulphate of oxide of chromium forms with the sulphates of potassa and ammonia double salts, which are exactly similar in form and composition to the preceding varieties of alum. They appear black by reflected, but ruby-red by transmitted light.

Manganese Alum.—Mitscherlich obtained this salt by mixing a solution of tersulphate of sesquioxide of manganese with sulphate of potassa, and evaporating to the consistence of syrup by a very gentle heat. On cooling, octohedral crystals of a browish-violet colour were deposited, which were similar in composition to common alum The tersulphate used for the purpose is prepared by macerating sesquioxide of manganese in very fine powder with strong sulphuric acid: it is made with difficulty, owing to the indisposition of that oxide to unite with acids, and to its ready conversion by heat into sulphate of the protoxide.

From the descriptions of the salts to which the term alum has been applied, it will be observed that they are characterized by two common properties: they all crystallize in the octohedral system, and they are all constituted as represented by the formula $RO,SO_3 + R_2O_3,3SO_3 + 24$ aq., where RO represents an eq. of potassa, or oxide of ammonium, and R_2O_3 any of the isomorphous oxides of aluminium, iron, manganese, and chromium. As Berzelius has ably remarked, the formula and crystalline form serve to determine the genus alum, and the oxidized bases its species.

Sulphate of Protoxide of Iron and Alumina.—This salt, which has recently been formed by Klauer, is obtained by the spontaneous evaporation of a mixture of sulphate of protoxide of iron and tersulphate of alumina in eq. proportions, a large excess of sulphuric acid being present (Lieb. An. xiv. 261). The salt is deposited in long acicular crystals, the constitution of which, being $FeO,SO_3 + Al_2O_3,3SO_3 + 24HO$, is similar to that of an alum; but as the crystals do not belong to the octohedral system, it has been improperly described as one of that class.

A compound, exactly analogous, in which protoxide of manganese is substituted for protoxide of iron, occurs native on the gold coast of Africa, in beautiful silvery fibres, many inches long. It has been described and analyzed by Apjohn, who found its formula to be $MnO,SO_3 + Al_2O_3,3SO_3 + 24HO$.

A similar salt of magnesia was obtained in the same manner; and it is exceedingly probable that a similar compound might be formed with the isomorphous oxides of zinc, copper, nickel, cobalt, and with lime. These, in their turn, might again be varied by substituting for the alumina the sesquioxides of iron, manganese, and chromium.

Anhydrous Sulphates with Ammonia.—Rose has observed that some sulphates possess the property of absorbing ammonia, and of forming with it definite compounds, which differ from sulphates of ammonia prepared in the moist way, both by containing no water of crystallization, and by the facility with which the alkali is again given out. They are formed by placing the anhydrous sulphate in a glass tube, and transmitting over it at common temperatures ammoniacal gas, well dried by fused potassa, as long as any increase of weight is observed: some sulphates absorb the gas very rapidly at first, and with disengagement of heat; but the absorption afterwards becomes slow, and requires a day or two in order to be complete. The salts most remarkable for this property are those which, in solution, are disposed to unite with ammonia.—Sulphate of protoxide of copper greedily absorbs ammonia, and acquires a deep blue colour similar to the ammoniaret of copper, prepared with moisture; but the former compound consists of 2 eq. of sulphate of protoxide of copper and 5 eq. of ammonia, while the latter contains 1 eq. of sulphate of copper, 2 of ammonia, and 1 eq. of water. Sulphate of protoxide of cobalt, as well as that of nickel, unites with 3 eq. of ammonia; that of zinc with 2·5, and that of manganese with 2 eq. The latter when heated loses all its ammonia, and returns to its original condition; whereas most of the other ammoniaco-sulphates suffer partial decomposition at the same time. Sulphate of oxide of silver unites with 1 eq. of ammonia; and a similar compound was prepared by C. G. Mitscherlich, but with 2 eq. of ammonia. With most of the other anhydrous sulphates ammonia refuses to unite.

On considering the nature of these compounds, one is at first disposed to associate them with double salts, supposing the acid to be divided between the two bases. But this opinion is rendered unlikely by the large quantity of combined ammonia, by the facility with which the alkali is given off, and by the absence of water, so constantly present in other ammoniacal sulphates. Rose, with much plausibility, compares these compounds to hydrates: water acts as a feeble base to saline compounds, combining with some in one or more proportions, and not at all with others, differing greatly in the ratio in which it combines with different salts, and being abandoned with great facility, often by mere exposure to the air. The same features characterise the combinations of ammonia with the anhydrous sulphates. (Pog. Annalen, xx. 149.)

The sulphates are not the only salts which absorb ammonia.

Rose found that the nitrate of oxide of silver unites with 3 eq. of ammonia, and the gas, if freely supplied, is at first absorbed with such rapidity, and the corresponding increase of temperature is so great, that the salt enters into fusion. Heat expels the ammonia before the nitrate of oxide of silver is decomposed. A similar compound, but with less ammonia, was formed by C. Mitscherlich.

SULPHITES.

The salts of sulphurous acid have not hitherto been minutely examined. The sulphites of potassa, soda, and ammonia, which are made by neutralizing those alkalies with sulphurous acid, are soluble in water; but most of the other sulphites, so far as is known, are of sparing solubility. The sulphites of baryta, strontia, and lime, are very insoluble; and consequently the soluble salts of these earths decompose the alkaline sulphites.

The stronger acids, such as the sulphuric, hydrochloric, phosphoric, and arsenic acids, decompose all the sulphites with effervescence, owing to the escape of sulphurous acid, which may easily be recognized by its odour. Nitric acid, by yielding oxygen, converts the sulphites into sulphates.

When the sulphites of the fixed alkalies and alkaline earths are strongly heated in close vessels, a sulphate is generated, and a portion of sulphur sublimed. In open vessels at a high temperature they absorb oxygen, and are converted into sulphates; and a similar change takes place even in the cold, especially when they are in solution. Gay-Lussac has remarked, that a neutral sulphite always forms a neutral sulphate when its acid is oxidized; a fact from which it may be inferred, that neutral sulphites consist of 1 eq. of the acid and 1 eq. of the base.

The hyposulphates and hyposulphites are of such little practical importance, that it is unnecessary to describe individual salts: their general character has been already given. For a particular description of the hyposulphates, the reader is referred to an essay by Heeren. (An. de Ch. et Ph. xl. 30.)

NITRATES.

The nitrates may be prepared by the action of nitric acid on metals, on the salifiable bases themselves, or on carbonates. As nitric acid forms soluble salts with all alkaline bases, the acid of the nitrates cannot be precipitated by any reagent. The are readily distinguished from other salts, however, by the characters already described.

All the nitrates are decomposed without exception by a high temperature; but the changes which ensue are modified by the nature of the oxide. Nitrate of oxide of palladium is decomposed at such a moderate temperature, that a great part of the acid passes off unchanged. Nitrate of oxide of lead requires a red heat, by which it is resolved, as already mentioned, into oxygen and nitrous acid. In some instances the changes are more complicated. With nitre, for example, nitrite of potassa is at first generated, with escape of oxygen gas: as the heat increases, the nitrous acid is resolved into binoxide of nitrogen and oxygen, the former of which remains in combination with potassa; the binoxide is then resolved into protoxide of nitrogen and oxygen, the former being retained by the alkali; and, lastly, nitrogen gas is disengaged, and peroxide of potassium remains. If the operation is performed in an earthen vessel,, the peroxide will be more or less decomposed, in consequence of the affinity of the earthy substances for potassa. The preceding facts have been chiefly collected from the observations of Phillips and Berzelius. The tendency of potassa and soda to unite with protoxide of nitrogen was first discovered by Davy; and Hess has lately remarked that similar compounds are obtained with soda, baryta, and lime, as well as potassa, when their nitrates are heated until the disengaged gas is found to extinguish a light.

As the nitrates are easily decomposed by heat alone, they must necessarily suffer decomposition by the united agency of heat and combustible matter. The nitrates on this account are much employed as oxidizing agents, and frequently act with greater efficacy even than nitro-hydrochloric acid. Thus metallic titanium, which resists the action of these acids, combines with oxygen when heated with nitre. The efficiency of this salt, which is the nitrate usually employed for the purpose, depends not only on the affinity of the combustible for oxygen, but likewise on that of the oxidized body for potassa. The process for oxidizing substances by means of nitre is called *deflagration*, and is generally performed by mixing the inflammable body with an equal weight of the nitrate, and projecting the mixture in small portions at a time into a red-hot crucible.

All the neutral nitrates of the fixed alkalies and alkaline earths, together with most of the neutral nitrates of the common metals, are composed of 1 eq. of nitric acid, and 1 eq. of a protoxide.

Consequently, the oxygen of the oxide and acid in all such salts must be in the ratio of 1 to 5, the general formula being $MO + NO_5$.

The only nitrates found native are those of potassa, soda, lime, and magnesia.

The composition of the principal nitrates is exhibited in the following table:—

Names.	Base.	Acid.	Equiv.	Formulæ.
Nitrate of Potassa	47·15 1 eq.	+54·15 1 eq.	=101·3	$KO+NO_5$.
——— Soda	31·3 1 eq.	+54·15 1 eq.	= 85·45	$NaO+NO_5$.
Oxide of Ammonium	17·15 1 eq.	+54·15 1 eq.	= 80·3	H_4NO+NO_5.
Nitrate of Baryta	76·7 1 eq.	+54·15 1 eq.	=130·85	$BaO+NO_5$.
——— Strontia	51·8 1 eq.	+54·15 1 eq.	=105·95	$SrO+NO_5$.
Do. in prisms with 45 or 5 eq. of water			=150·95	
Nitrate of Lime	28·5 1 eq.	+54·15 1 eq.	= 82·65	$CaO+NO_5$.
——— Magnesia	20·7 1 eq.	+54·15 1 eq.	= 74·85	$MgO+NO_5$.
——— Protox. Copper	39·6 1 eq.	+54·15 1 eq.	= 93·75	$CuO+NO_5$.
Do. in prisms with 63 or 7 eq. of water?			=156·75	
Nitrate of protox. Lead	111·6 1 eq.	+54·15 1 eq.	=165·75	$PbO+NO_5$.
Dinitrate of ditto	223·2 2 eq.	+54·15 1 eq.	=277·35	$2PbO+NO_5$.
Nitrate of protox. Mercury	210 1 eq.	+54·15 1 eq.	=264·15	$HgO+NO_5$.
Do. in crystals with 18 or 2 eq. of water			=282·15	
Nitrate of perox. Mercury	218 1 eq.	+54·15 1 eq.	=272·15	HgO_2+NO_5.
Dinitrate do.	436 2 eq.	+54·15 1 eq.	=490·15	$2HgO_2+NO_5$.
Nitrate of ox. Silver	116 1 eq.	+54·15 1 eq.	=170·15	$AgO+NO_5$.

Nitrate of Potassa.—This salt is generated spontaneously in the soil, and crystallizes upon its surface, in several parts of the world, and especially in the East Indies, whence the greater part of the nitre used in Britain is derived. In some parts of the Continent, it is prepared artificially from a mixture of common mould or porous calcareous earth with animal and vegetable remains containing nitrogen. When a heap of these materials, preserved moist and in a shady situation, is moderately exposed to the air, nitric acid is gradually generated, and unites with the potassa, lime, and magnesia, which are commonly present in the mixture. On dissolving these salts in water, and precipitating the two earths by carbonate of potassa, a solution is formed, which yields crystals of nitre by evaporation. The nitric acid is possibly generated under these circumstances by the nitrogen of the organic matters combining during putrefaction with oxygen of the atmosphere, a change which must be attributed to the affinity of oxygen for nitrogen, aided by that of nitric acid for alkaline bases. The nitre made in France is often said to be formed by this process; but the greater part is certainly obtained by lixiviation from certain kinds of plaster of old houses, where nitrate of lime is gradually generated. Liebig, in his profound work on the application of organic chemistry to Agriculture and Physiology, has rendered it highly probable, if not certain, that the nitric acid is formed by the oxidation of ammonia, which exists in the atmosphere, and is brought by absorption in contact with organic matters in a state of slow combustion or *eremacausis.* Ammonia is more easily oxidized than any other compound of nitrogen; probably because it contains hydrogen, the oxidation of which yields water, which is essential to the existence of nitric acid. Animal matters only act as a source of ammonia, and nitric acid may be formed where the decaying organic matter contains no nitrogen, from the ammonia present in the atmosphere. For the details of his argument I must refer to Dr. Playfair's translation of the above work recently (Sept. 1840) published.

Nitrate of potassa is a colourless salt, which crystallizes readily in six-sided prisms. Its taste is saline, accompanied with an impression of coolness. It requires for solution seven parts of water at 60°, and its own weight of boiling water. It contains no water of crystallization, but its crystals are never quite free from water lodged mechanically within them. At 616° it undergoes the igneous fusion, and like all the nitrates, is decomposed by a red heat.

Nitre is chiefly employed in chemistry as an oxidizing agent, and in the formation of nitric acid. Its chief use in the arts is in making gunpowder, which is a mixture of nitre, charcoal, and sulphur. In the East Indies it is employed for the preparation of cooling mixtures; an ounce of powdered nitre dissolved in five ounces of water reduces its temperature by fifteen degrees. It possesses powerful antiseptic properties, and is therefore much employed in the preservation of meat and animal matters in general.

Nitrate of Soda.—This salt is analogous in its chemical properties to the preceding compound. It sometimes crystallizes in oblique rhombic prisms; but it more commonly occurs as an obtuse rhombohedron. (Brooke.) It is plentifully found in the soil in some parts of India; and at Atacama in Peru it covers large districts, and occurs in immense quantity. With charcoal and sulphur it forms a mixture which burns much slower than common gunpowder, and therefore cannot be substituted for nitre; but it may be advantageously used in the manufacture both of sulphuric and nitric acid. It is disposed to deliquesce in the air, and is soluble in twice its weight of cold water, and still more freely by the aid of heat.

Nitrate of Oxide of Ammonium.—It may be formed by neutralizing dilute nitric acid by carbonate of ammonia, and evaporating the solution. This salt may be procured in three different states, which have been described by Davy. (Researches concerning the nitrous oxide.) If the evaporation is conducted at a temperature not exceeding 100°, the salt is obtained in prismatic crystals isomorphous with nitre. If the solution is evaporated at 212°, fibrous crystals are procured; and if the heat be gradually increased to 300°, it forms a brittle compact mass on cooling. The fibrous and compact varieties still contain water, the former 8·2 per cent. and the latter 5·7. All these varieties deliquesce in a moist air, and are very soluble in water.

The change which nitrate of ammonia undergoes at a temperature varying between 400° and 500° has already been explained. When heated to 600°, it explodes with violence, being resolved into water, nitrous acid, binoxide of nitrogen, and nitrogen. The fibrous variety was found by Davy to yield the largest quantity of protoxide of nitrogen. From one pound of this salt he procured nearly three cubic feet of the gas.

Nitrate of Baryta.—This salt is sometimes used as a reagent and for preparing pure baryta. It is easily prepared by digesting the native carbonate, reduced to powder, in nitric acid diluted with 8 or 10 times its weight of water. The salt crystallizes readily by evaporation in transparent anhydrous octohedrons, and is very apt to decrepitate by heat unless previously reduced to powder. It requires 12 parts of water at 60° and 3 or 4 of boiling water for solution, but is insoluble in alcohol. It undergoes the igneous fusion in the fire before being decomposed.

Nitrate of Strontia.—This salt may be made from strontianite in the same manner as the foregoing compound, to which it is exceedingly analogous. It commonly crystallizes in anhydrous octohedrons which undergo no change in a moderately dry atmosphere, and are insoluble in alcohol; but sometimes it contains 30 per cent. of water of crystallization, and then assumes the form of the oblique prismatic system.

Nitrates of Lime and Magnesia.—These salts crystallize in hydrated prisms when their solutions are concentrated to the consistence of syrup, but the quantity of water which they contain is not ascertained. They deliquesce rapidly in the air, are very soluble in water, and are dissolved by alcohol, the nitrate of lime more freely than nitrate of magnesia.

Nitrate of Protoxide of Copper.—This salt is prepared by the action of nitric acid on copper. It crystallizes, though with some difficulty, in prisms of a deep blue colour, which are very soluble in water and alcohol, and deliquesce on exposure to the air. The green insoluble subsalt, procured by exposing the neutral nitrate to a heat of 400°, or by dropping an alkali into a solution of that salt, the latter being in excess, is a trinitrate, consisting of 3 eq. of oxide of copper, 1 eq. of acid, and 1 eq. of water. From the observations of Graham, the neutral salt contains 3 eq. of constitutional water, and therefore may be represented by the formula $CuO, NO_5, 3HO$: from this it would appear that the subsalt is similarly constituted, being a nitrate of water with 3 eq. of constitutional oxide of copper. It is on this supposition represented by the formula $HO, NO_5, 3CuO$. It is probable that the nitrates of lime and magnesia are similarly constituted, as has been shown to be the case with nitric acid of sp. gr. 1·42. When heated to redness it yields pure oxide of copper.

Nitrate of Protoxide of Lead.—This salt is formed by digesting litharge in dilute nitric acid, and crystallizes readily in octohedrons, which are anhydrous and almost always opaque. It has an acid reaction, but is neutral in composition.

A dinitrate was formed by Berzelius by adding to a solution of the neutral nitrate a quantity of pure ammonia insufficient for separating the whole of the acid.

Nitrates of the Oxides of Mercury.—The protonitrate is conveniently formed by digesting mercury in nitric acid diluted with three or four parts of water, until the acid is saturated, and then allowing the solution to evaporate spontaneously in an open vessel. The solution always contains, at first, some nitrate of the peroxide; but if metallic mercury is left in the liquid, a pure protonitrate is gradually deposited. The salt thus formed has hitherto been regarded as the neutral protonitrate; but according to the analysis of M. C. Mitscherlich (Pog. Annalen, ix. 387), it is a subsalt, in which the protoxide and acid are in the ratio of 208 to 36. This result, however, requires confirmation. The neutral protonitrate is said by C. Mitscherlich to be obtained in crystals, by dissolving the former salt in pure water acidulated with nitric acid, and evaporating spontaneously without the contact of metallic mercury or uncombined oxide. These salts dissolve completely in water slightly acidulated with nitric acid, but in pure water a small quantity of a yellow subsalt is generated.

When mercury is heated in an excess of strong nitric acid, it is dissolved with brisk effervescence, owing to the escape of binoxide of nitrogen, and transparent prismatic crystals of the pernitrate are deposited as the solution cools. When put into hot water it is resolved into a soluble salt, the composition of which is unknown, and into a yellow dinatrate of the peroxide. (An. de Ch. et Phys. xix.)

Nitrate of Oxide of Silver.— Silver is readily oxidized and dissolved by nitric acid diluted with two or three times its weight of water, forming a solution which yields transparent tabular crystals by evaporation. These crystals, which are anhydrous, undergo the igneous fusion at 426°, and yield a crystalline mass in cooling; but when the temperature reaches 600° or 700°, complete decomposition ensues, the acid being resolved into oxygen and nitrous acid, while metallic silver is left. When liquefied by heat, and received in small cylindrical moulds, it forms the *lapis infernalis* or *lunar caustic*, employed by surgeons as a cautery. The nitric acid appears to be the agent which destroys the animal texture, and the black stain is owing to the separation of oxide of silver. It is sometimes employed for giving a black colour to the hair, and is the basis of the indelible ink for marking linen.

The pure nitrate, whether fused or in crystals, is colourless and transparent, and does not deliquesce by exposure to the air; but common lunar caustic is dark and opaque, and dissolves imperfectly in water, owing to some of the nitrate being decomposed during its preparation. It is impure also, always containing nitrate of protoxide of copper, and frequently traces of gold. The pure salt is soluble in its own weight of cold, and in half its weight of hot water. It dissolves also in four times its weight of alcohol. Its aqueous solution, if preserved in clean glass vessels, especially with the addition of a minute quantity of free nitric acid, undergoes little or no change even in the direct solar rays; but when exposed to light, especially to sunshine, in contact with paper, the skin, or any organic substance, a black stain is quickly produced, owing to decomposition of the salt and reduction of its oxide to the metallic state. This change is so constant, that nitrate of oxide of silver constitutes an extremely delicate test of the presence of organic matter, and has been properly recommended as such by Dr. Davy. Its solution is always kept in the laboratory as a test for chlorine and hydrochloric acid.

Nitrate of oxide of silver, even after fusion, reddens vegetable colouring matters; but it is quite neutral in composition.

NITRITES.

Little is known with certainty concerning the compounds of nitrous acid with alkaline bases. Nitrite of potassa is formed by heating nitre to redness, and removing it from the fire before the decomposition is complete. On adding a strong acid to the product, red fumes of nitrous acid are disengaged, a character which is common to all the nitrites. The nitrite of soda, baryta, and strontia, may be obtained in the same manner, and doubtless several others. Two nitrites of oxide of lead have been described in the Annales de Chimie, lxxxiii. by Chevreul and Berzelius. It is possible, however, that these compounds are hyponitrites.

CHLORATES.

The salts of chloric acid are very analogous to the nitrates. As the chlorates of the alkalies, alkaline earths, and most of the common metals, are composed of 1 eq. of chloric acid and 1 eq. of a protoxide, $MO + ClO_5$, it follows that the oxygen of the latter to that of the former is in the ratio of 1 to 5. The chlorates are decomposed by a red heat, nearly all of them being converted into metallic chlorides, with evolution of pure oxygen gas. They deflagrate with inflammable substances with greater violence than nitrates, yielding oxygen with such facility that an explosion is produced by slight causes. Thus, a mixture of sulphur with three times its weight of chlorate of potassa explodes when struck between two hard surfaces. With charcoal and the sulphurets of arsenic and antimony, this salt forms similar explosive mixtures; and with phosphorus it detonates violently by percussion. One of the mixtures, employed in the percussion locks for guns, consists of sulphur and chlorate of potassa, with which a little charcoal or gunpowder is mixed; but as the use of these materials is found corrosive to the lock, fulminating mercury is now generally preferred.

All the chlorates hitherto examined are soluble in water, excepting the chlorate of protoxide of mercury, which is of sparing solubility. These salts are distinguished by the action of strong hydrochloric and sulphuric acids, the former of which occasions the disengagement of chlorine and protoxide of chlorine, and the latter of peroxide of chlorine.

None of the chlorates are found native, and the only ones that require particular description are those of potassa and baryta.

Chlorate of Potassa.—This salt, formerly called *oxymuriate* or *hyper-oxymuriate of potash*, is colourless, and crystallizes in four and six-sided scales of a pearly lustre. Its forms are stated by Brooke to belong to the oblique prismatic system. It is soluble in sixteen times its weight of water at 60°, and in two and a half of boiling water. It is quite anhydrous, and when exposed to a temperature of 400° or 500° undergoes the igneous fusion. On increasing the heat almost to redness, effervescence ensues, and pure oxygen gas is disengaged, phenomena which have been explained in the section on oxygen. It can bear a heat of 600° without decomposition.

Chlorate of potassa is made by transmitting chlorine gas through a concentrated solution of pure potassa, until the alkali is completely neutralized. The solution which, after being boiled for a few minutes, contains nothing but chloride of potassium and chlorate of potassa, is gently evaporated till a pellicle forms upon its surface, and is then allowed to cool. The greater part of the chlorate crystallizes, while the chloride remains in solution. The crystals, after being washed with cold water, may be purified by a second crystallization.

Chlorate of Baryta is of interest, as being the compound employed in the formation of chloric acid; and the readiest mode of preparing it is by the process of Wheeler. On digesting for a few minutes a concentrated solution of chlorate of potassa with a slight excess of silicated hydrofluoric acid, the alkali is precipitated in the form of an insoluble double fluoride of silicium and potassium, while chloric acid remains in solution. The liquid after filtration is neutralized by carbonate of baryta, which throws down the excess of silicated hydrofluoric acid, and chlorate of baryta is left in solution. By evaporation it yields prismatic crystals, which require for solution 4 times their weight of cold, and a still smaller quantity of hot water. They are composed of 76·7 parts or 1 eq. of baryta, 75·42 or 1 eq. of chloric acid, and 9 or 1 eq. of water.

Perchlorates.—The neutral proto-salts of perchloric acid consist of 1 eq. of acid and base, as is expressed by the formula $MO + Cl_2O_7$. Most of these salts are deliquescent, very soluble in water, and soluble in alcohol: four only were found by Serullas to be not deliquescent,—the perchlorates of potassa, ammonia, protoxide of lead, and protoxide of mercury. When heated to redness they yield oxygen gas and metallic chlorides; and they are distinguished from the chlorates by not acquiring a yellow tint on the addition of hydrochloric acid. The perchlorate of potash is prepared from the chlorate by the action of heat or sulphuric acid, as already mentioned. It is the most insoluble of the perchlorates, and on this account perchloric acid precipitates potassa from its salts, being a test of about the same delicacy as tartaric acid. The other perchlorates are made by neutralizing the base with perchloric acid. The solubility in alcohol of the perchlorates of baryta, soda, and oxide of silver, is a property which the analytical chemist may avail himself of in analysis for the separation of potassa and soda from each other.

CHLORITES.

The alkaline salts of chlorous acid are readily made, as mentioned at page 285, by transmitting a current of chlorous acid gas into a solution of the pure alkalies. All that have as yet been examined are soluble in water, and are remarkable for their highly bleaching and oxidizing properties. By the latter properties and the evolution of chlorous acid on the addition of any of the stronger acids their presence is readily recognized.

Hypochlorites.—The hypochlorites may be produced by the action of chlorine gas on the salifiable bases. The most important of them is the hypochlorite of lime, the well-known bleaching powder, which has commonly been described as the oxymuriate or chloride of lime. It is prepared for commercial purposes by exposing thin strata of recently-slaked lime in fine powder to an atmosphere of chlorine. The gas is absorbed in large quantity, and the chloride of calcium and hypochlorite of lime are produced in equivalent proportions.

It is a dry white powder, which smells faintly of chlorine, and has a strong taste. It dissolves partially in water, and the solution possesses powerful bleaching properties, and contains both chlorine and lime; while the undissolved portion is hydrate of lime, retaining a small quantity of chlorine. The aqueous solution, when exposed to the atmosphere, is gradually decomposed; chlorine is set free, and carbonate of lime generated. On boiling the liquid, chloride of calcium and, I presume, chlorate of lime are formed; and by long keeping, the dry chloride appears to undergo a similar change,—at least chloride of calcium is produced in large quantity. It is also decomposed by a strong heat: at first, chlorine is evolved; but pure oxygen is afterwards disengaged, and chloride of calcium remains in the retort.

The composition of chloride of lime was first carefully investigated by Dalton,* and it has since been analyzed by Thomson,† Welter,‡ and Ure.§ The three first-mentioned chemists infer from their researches that bleaching powder is a hydrated *sub-chloride* or *dichloride* of lime, in which one equivalent of chlorine is united with two equivalents of lime. They are also of opinion, that on mixing this dichloride with water, the chloride is dissolved, and one equivalent of lime separated as an insoluble powder. Dr. Ure, on the contrary, denies that bleaching powder is a dichloride, and maintains that the elements of this powder do not constitute a regular atomic combination. He found that the quantity of chlorine absorbed by hydrate of lime is variable, depending not only on the pressure and degree of exposure, but on the quantity of water present. From these experiments it appears that the commercial bleaching powder is essentially a hypochlorite with single equivalents of its elements, but mixed with variable quantities of hydrate of lime.

According to Millon, bleaching-powder is an oxychloride of calcium, $\mathrm{Ca}\left.\begin{matrix}\mathrm{Cl}\\ \mathrm{O}\end{matrix}\right\} = \mathrm{CaO,\ ClO} + \mathrm{CaCl}$. It is now certain, that even if hypochlorites exist, the bleaching compounds of lime, potash, and soda contain the chlorides of these metals as an essential constituent, according to the second of the above formulæ. But according to the view of Millon, these compounds must be viewed as oxychlorides, corresponding to the peroxides of the metals, in which part of the oxygen is replaced by chlorine. The peroxides of sodium and calcium are NaO_2 and CaO_2, and the bleaching compounds are $\mathrm{Na}\left.\begin{matrix}\mathrm{Cl}\\ \mathrm{O}\end{matrix}\right\}$ and $\mathrm{Ca}\left.\begin{matrix}\mathrm{Cl}\\ \mathrm{O}\end{matrix}\right\}$. But the peroxide of potassium is KO_3, and consequently its bleaching compound ought to be $\mathrm{K}\left.\begin{matrix}\mathrm{Cl_2}\\ \mathrm{O}\end{matrix}\right\}$. In point of fact, it contains twice as much chlorine as the corresponding compound of sodium, which renders this view extremely probable. Similar oxychlorides are formed by adding these compounds to solutions of lead, iron, and copper;

---

* Annals of Philosophy, i. 15, and ii. 6.

† Ibid. xv. 401.

‡ Ann. de Ch. et Ph. vol. viii.

§ Quarterly Journal, xiii. 1.

and by the action of these compounds on hydrochloric acid, Millon has obtained a new bleaching compound, perchloride of hydrogen, HCl_2, perfectly analogous to peroxide of hydrogen, which is the type of the class of bodies just described, as well as of the superoxides of the metals, its formula being $H\left.\begin{matrix}O\\O\end{matrix}\right\}$. For details, the reader is referred to Millon's paper in the Journal de Pharmacie for September 1839, p. 595.

Several methods have been proposed for estimating the value of different specimens of bleaching powder. Perhaps the most convenient for the artist is that of Welter, which consists in ascertaining the power of the bleaching liquid to deprive a solution of indigo of known strength of its colour; and directions have been drawn up by Gay-Lussac for enabling manufacturers to employ this method with accuracy. (Annals of Philosophy, xxiv. 218.) For analytical purposes, the best method is to decompose chloride of lime, confined in a glass tube over mercury, by means of hydrochloric acid. Chloride of calcium is generated, and the chlorine being set free, its quantity may easily be measured.

IODATES.

From the close analogy in the composition of chloric and iodic acids, it follows that the general character of the iodates must be similar to that of the chlorates. Thus in all neutral protiodates the oxygen contained in the oxide and acid is in the ratio of 1 to 5. They form deflagrating mixtures with combustible matters; and on being heated to low redness, oxygen gas is disengaged and a metallic iodide remains. As the affinity of iodine for metals is less energetic than that of chlorine, many of the iodates part with iodine as well as oxygen when heated, especially if a high temperature is employed.

The iodates are easily recognized by the facility with which their acid is decomposed by deoxidizing agents. Thus, the sulphurous, phosphorous, hydrochloric, and hydriodic acids, deprive iodic acid of its oxygen, and set iodine at liberty. Hydrosulphuric acid not only decomposes the acid of these salts, but occasions the formation of hydriodic acid by yielding hydrogen to the iodine. Hence an iodate of potassa may be converted into the iodide by transmitting a current of hydrosulphuric acid gas through its solution. None of the iodates have been found native. They are all of very sparing solubility, or actually insoluble in water, excepting the iodates of the alkalies.

Iodate of Potassa.—This salt may be procured by adding iodine to a concentrated hot solution of pure potassa, until the alkali is completely neutralized. The liquid, which contains an iodate and iodide, is evaporated to dryness by a gentle heat, and the residue, when cold, is treated by repeated portions of boiling alcohol. The iodate, which is insoluble in that menstruum, is left, while the iodide of potassium is dissolved. A better process has been recommended by M. Henry, jun., founded on the property which iodide of potassium possesses, of absorbing oxygen while in the act of escape from decomposing chlorate of potassa. For this purpose iodide of potassium is fused in a capacious hessian crucible, and when, after removal from the fire, it is yet semi-fluid, successive portions of pulverized chlorate of potassa are projected into it, stirring well after each addition. The materials froth up considerably, and when the action is over, a white, opaque, cellular mass remains, easily separable from the crucible: tepid water dissolves out the chloride of potassium, and leaves the iodate. Convenient proportions are one part of iodide of potassium and rather more than one and a half of chlorate of potassa. (Journ. de Pharmacie, July 1832.)

All the insoluble iodates may be procured from this salt by double decomposition. Thus iodate of baryta may be formed by mixing chloride of barium with a solution of iodate of potassa.

A biniodate of potassa has been described by Serullas. It is formed by incompletely neutralizing a hot solution of chloride of iodine with potassa or its carbonate, and setting it aside to cool. A peculiar compound of chloride of potassium and biniodate of potassa falls; but on dissolving this substance, filtering and exposing the solution to a temperature of 77°, the biniodate is gradually deposited in right rhombic prisms terminated by dihedral summits. It is soluble in 75 times its weight of water at 59°.

A teriodate may be formed by mixing a large excess of sulphuric acid with a moderately dilute solution of iodate of potassa. On evaporating at 77°, the teriodate is deposited in regular rhomboidal crystals, which require 25 times their weight of water at 60° for solution.

Serullas states that the compound of chloride of potassium and biniodate of potassa, above mentioned, may be formed by the action of hydrochloric acid on iodate of potassa. By spontaneous evaporation it is obtained, sometimes in brilliant, transparent, elongated prisms, and at other times in hexagonal laminæ; but generally it crystallizes in right quadrangular prisms with their lateral edges truncated, and terminated by four-sided summits. (An. de Ch. et Ph. xliii. 113.)

Bromates.—These compounds have many characters in common with the chlorates and iodates; but hitherto they have been but partially examined.

PHOSPHATES.

In studying these salts, the reader must bear in mind that there are three isomeric modifications of the same acid, which have been described under the names of *phosphoric*, *pyrophosphoric*, and *metaphosphoric acid;* and therefore it will be necessary to have three corresponding families of salts, the *phosphates*, *pyrophosphates*, and *metaphosphates.* This distinction, and the other facts lately recorded by Graham, render it necessary either to change the names of the phosphates, or to retain their old names in opposition to the principles of nomenclature. The most consistent conduct will be to describe each salt under its scientific name, and add at the same time its ordinary one. An eq. of each of the three acids, is a compound of 31·4 parts or 2 eq. of phosphorus + 40 parts or 5 eq. of oxygen = 71·4, expressed by the formula P_2O_5. To form a salt *neutral in composition*, 1 eq. of an alkaline base is requisite; and in the case of any protoxide, indicated by MO, the general formula will be $MO + P_2O_5$. If 2 eq. of a protoxide are united with one of the acid, we have a *disalt*, $2MO + P_2O_5$; and if 3 eq. of a base combine with 1 eq. of the acid, it is a *trisalt*, $3MO + P_2O_5$. It seems also that water plays the part of an alkaline base towards each of the three acids, either alone or conjointly with another base: the salts with such compound bases can scarcely be viewed in the light of double salts, since the two bases act together as one electro-positive element.

All the protophosphates which are neutral in composition are soluble in water, and redden litmus paper; whence they are commonly called superphosphates. The triphosphates, except those of the pure alkalies, are either sparingly soluble or insoluble in water; but they are all dissolved by dilute nitric or phosphoric acid, being converted into the soluble phosphates. All the triphosphates with fixed and strong bases bear a red heat without change; but the phosphates and diphosphates, to judge from experiments on the soda salts, are converted into metaphosphates and pyrophosphates. Most of the phosphates of the second class of metals are resolved into phosphurets by the conjoint agency of heat and combustible matter. The phosphates of the alkalies are only partially decomposed under these circumstances, and the phosphates of baryta, strontia, and lime, undergo no change.

The presence of a soluble phosphate may be distinguished by the tests already mentioned for phosphoric acid. The insoluble phosphates are decomposed when boiled with a strong solution of carbonate of potassa or soda, the acid uniting with the alkali so as to form a soluble phosphate: the earthy phosphates, indeed, are decomposed with difficulty, requiring continued ebullition, and should preferably be fused with an alkaline carbonate, like an insoluble sulphate.

Several phosphates are met with in nature, such as those of lime, alumina, and the oxides of manganese, iron, uranium, copper, and lead.

The composition of the principal phosphates is given in the following table:—

Names.	Base.			Acid.		Equiv.	Formulæ.
Triphosphate of Soda .		93·9	3 eq.	+ 71·4	1 eq.	=165·3	$3NO+P_2O_5$.
Do. in crystals with 216 or 24 eq. of water . .						=381·3	
Triphosph. Soda and Basic Water .	Soda Water	62·6 9	2 eq. 1 eq.	+ 71·4	1 eq.	=143	$2NaO,HO+P_2O_5$.
Do. in crystals with 216 or 24 eq. of water . .						=359	
Do. . . 135 or 15 eq. of water . .						=278	
Acid Triphos. Soda and Basic Water	Soda Water	31·3 18	1 eq. 2 eq.	+ 71·4	1 eq.	=120·7	$NaO,2HO+P_2O_5$.
Do. in crystals with 18 or 2 eq. of water . .						=138·7	
Triphosphate of Potassa .		141·45	3 eq.	+ 71·4	1 eq.	=212·85	$3KO+P_2O_5$.
Triphosph. of Potassa and Basic Water	KO HO	94·3 9	2 eq. 1 eq.	+ 71·4	1 eq.	=174·7	$2KO,HO+P_2O_5$.
Acid Triphosphate ditto . .	Potassa Water	47·15 18	1 eq. 2 eq.	+ 71·4	1 eq.	=136·55	$KO,2HO+P_2O_5$.
Triphosph. of Soda, Oxide Ammonium, and Basic Water	Soda Ox.Am. Water	31·3 26·15 9	1 eq. 1 eq. 1 eq.	+ 71·4	1 eq.	=137·85	$NaO,H_4NO,HO+P_2O_5$.
Do. in crystals with 72 or 8 eq. of water . .						=209·85	
Triphos. of oxide of Am. & Basic Water	Ox.Am. Water	52·30 9	2 eq. 1 eq.	+ 71·4	1 eq.	=132·70	$2H_4NO,HO+P_2O_5$.
Acid Triphosphate ditto . .	Ox.Am. Water	26·15 18	1 eq. 2 eq.	+ 71·4	1 eq.	=115·55	$H_4NO,2HO+P_2O_5$.
Bone Phosphate of Lime .		228	8 eq.	+214·2	3 eq.	=442·2	$8CaO+3P_2O_5$.
Triphosphate do. . . .		85·5	3 eq.	+ 71·4	1 eq.	=156·9	$3CaO+P_2O_5$.
Triphos. of Lime and Basic Water .	Lime Water	57 9	2 eq. 1 eq.	+ 71·4	1 eq.	=127·4	$2CaO,HO+P_2O_5$.
Acid Triphos. do.	Lime Water	28·5 18	1 eq. 2 eq.	+ 71·4	1 eq.	=117·9	$CaO,2HO+P_2O_5$.

For the new and more simple views of the constitution of the phosphates, pyrophosphates, and metaphosphates, which are becoming prevalent, the reader is referred to the account of them given in the general section on salts.

The triphosphate of baryta, strontia, protoxides of manganese, iron, copper, lead, silver, &c. precisely correspond to the triphosphate of lime, simply substituting 3 eq. of those oxides. These oxides in like manner form soluble phosphates analogous in composition to that of lime.

Triphosphate of Soda.—This salt, described by Graham as the *subsesquiphosphate*, is made by adding pure soda to a solution of the succeeding compound until the liquid feels soapy to the fingers, an excess of soda not being injurious. The liquid is then evaporated until a pellicle appears, and the crystals which form on cooling are quickly redissolved in water and recrystallized. Though the crystals do not change in the air, the solution absorbs carbonic acid, and the resulting carbonate of soda adheres to the triphosphate.

This salt crystallizes in colourless six-sided slender prisms, which have a strong alkaline taste and reaction, require 5 times their weight of water at 60°, and still less of hot water, for solution, and at 170° fuse in their water of crystallization. They may be exposed to a red heat without losing the characters of a phosphate. The feeblest acids deprive the salt of one-third of its soda.

When this salt is mixed in solution with nitrate of oxide of silver in excess, there is an exact interchange of elements, such that

1 eq. Triphosphate of Soda	$3NO+P_2O_5$	yield	1 eq. Triphosph. of Silver	$3AgO+P_2O_5$
& 3 eq. Nitrate of Silver	$3(AgO+NO_5$.		& 3 eq. Nitrate of Soda	$3(NaO+NO_5$.

The resulting solution is therefore quite neutral. The triphosphate of oxide of lead, and other insoluble triphosphates, may be prepared in like manner.

Triphosphate of Soda and Basic Water.—This salt is the most common of the phosphates, being manufactured on a large scale by neutralizing with carbonate of soda the acid phosphate of lime procured by the action of sulphuric acid on burned bones. It is generally described as the neutral phosphate of soda, and for distinction's sake is sometimes termed *rhombic phosphate*, from its crystals having the form of oblique rhombic prisms.

This salt crystallizes best out of an alkaline solution; but however prepared, it is always alkaline to test paper, and requires a considerable quantity of acid before losing its alkalinity. The crystals effloresce on exposure to the air, and require 4 times their weight of cold, and twice their weight of hot water for solution. It often contains traces of sulphuric acid, from which it may be purified by repeated solution and crystallization. When mixed with nitrate of oxide of silver, the interchange of elements is such that

1 eq. Rhombic Phos. 2 $NaO,HO+P_2O_5$ yeld 1 eq. Triphosph. of Silver $3AgO+P_2O_5$
& 3 eq. Nitrate of Silver $3(AgO+NO_5)$ & 2 eq. Nitrate of Soda $2(NaO+NO_5)$.

The yellow triphosphate of oxide of silver falls exactly as with the former salt, but 1 eq. of nitric acid is left free in the solution.

When a solution of the rhombic phosphate is evaporated at a temperature of 90°, it crystallizes with 14 instead of 24 equivalents of water, and the crystals differ, as might be expected, from the other salt in figure, and are permanent in the air. Both salts lose their basic water at a red heat, and are converted into a pyrophosphate.

Acid Triphosphate of Soda and Water.—This salt, commonly called *biphosphate of soda* from its acid reaction, may be formed by adding phosphoric acid to a solution of carbonate of soda, or to either of the preceding phosphates, until it ceases to give a precipitate with chloride of barium. Being very soluble in water, the solution must be concentrated in order that it may crystallize. This salt is capable of yielding two different kinds of crystals without varying its composition. The more unusual form, isomorphous with binarseniate of soda, is a right rhombic prism, the smaller lateral edge of which is 78° 30′, terminated by pyramidal planes. The form of its ordinary crystals is a right rhombic prism, the larger angle of which is 93° 54′.

The crystals of this salt consist, as stated at page 628, of $NaO, 2HO,P_2O_5 + 2HO$. When heated to 212°, the water of crystallization is expelled, and the anhydrous salt remains, still yielding a yellow precipitate with silver when neutralized by ammonia; but if exposed to a heat of 400°, it loses half its basic water, being reduced to NaO,HO,P_2O_5, and has the character of pyrophosphate of soda. At a red heat it is converted into metaphosphate of soda.

Triphosphate of Potassa.—Graham formed this salt by adding caustic potassa in excess to a solution of phosphoric acid, as well as by fusing phosphoric acid with a slight excess of carbonate of potassa. He obtained it in acicular crystals, which were very soluble in water, but not deliquescent.

Triphosphate of Potassa and Basic Water.—This salt may be prepared by neutralizing the superphosphate of lime from bones with carbonate of potassa. It is deliquescent, and has not been obtained in regular crystals.

Acid Triphosphate of Potassa and Basic Water may be formed by adding phosphoric acid to carbonate of potassa until the liquid ceases to give a precipitate with chloride of barium, and setting it aside to crystallize. The crystals belong to the square prismatic system, and they usually occur in square prisms terminated by the planes of an octohedron. They are acid to test paper.

When this compound is neutralized by carbonate of soda, and the solution set to crystallize, a phosphate of soda and potassa is deposited in crystals, the form of which is an oblique rhombic prism, which frequently occurs without any modification.

Triphosphate of Soda and Oxide of Ammonia and Basic Water.—This salt is easily prepared by mixing together 1 eq. of hydrochlorate of ammonia and 2 eq. of the rhombic phosphate of soda, each being previously dissolved in a small quantity of boiling water. As the liquid cools, prismatic crystals of the double phosphate are deposited, while chloride of sodium remains in solution. Their form is an oblique rhombic prism. This salt has been long known by the name of *microcosmic salt*, and is much employed as a flux in experiments with the blowpipe. When heated it parts with its water and ammonia, and a very fusible metaphosphate of soda remains.

Triphosphate of Ox. Ammonium and Basic Water.—This salt is formed by adding ammonia to concentrated phosphoric acid until a precipitate appears. On applying heat, the precipitate is dissolved, and on abandoning the solution to itself, the neutral salt crystallizes. The form of the crystals is an oblique rhombic prism, the smaller angle of which is 84° 30′. They often occur in rhombic prisms with diedral summits. (Mitscherlich.)

The acid triphosphate is made in the same manner as the preceding triphosphate of potassa. The crystals are less soluble than the preceding salt, and undergo no change on exposure to the air. Their form is an octohedron with a square base; but the right square prism, terminated by the faces of the octohedron, is the most frequent.

Phosphates of Lime.—The peculiar compound called the *bone phosphate*, exists in bones after calcination, and falls as a gelatinous precipitate on pouring chloride of calcium into a solution of the rhombic phosphate of soda, or on adding ammonia to a solution of any phosphate of lime in acids.

Triphosphate of Lime and Basic Water, commonly called *neutral phosphate*, falls as a granular precipitate, consisting of fine crystalline particles, when the rhombic phosphate of soda is added in solution drop by drop to chloride of calcium in excess. The residual liquid reddens litmus, owing to a small quantity of triphosphate of lime being generated.

Triphosphate of Lime cannot be formed by precipitation, but occurs in hexagonal prisms in the mineral called *apatite.*

Acid Triphosphate of Lime and Basic Water, called the *biphosphate* from its acid reaction, is formed by dissolving either of the preceding salts in a slight excess of phosphoric acid. The compound is deliquescent, very soluble, and crystallizes with great difficulty. It exists in the urine. The solution formed by the action of sulphuric acid on bones is probably a compound of lime with 2 or more eq. of phosphoric acid, being really a *superphosphate.*

Triphosphate of Magnesia and Basic Water.—It is formed by mixing together hot saturated solutions of the rhombic phosphate of soda and sulphate of magnesia, and separates on cooling in small crystals which contain 13 eq. of water to one of the salt. The triphosphate of magnesia is principally formed when the solutions are intermixed in the cold. These salts have been but little examined.

The phosphate of ammonia and magnesia subsides as a pulverulent granular precipitate from neutral or alkaline solutions, containing phosphoric acid, ammonia, and magnesia. It is readily dissolved by acids, and is sparingly soluble in pure water, especially when carbonic acid is present; but it is insoluble in a solution of most neutral salts, such as hydrochlorate of ammonia. It constitutes one variety of urinary concretions. According to Berzelius it consists of

Phosphoric Acid . .	71·4	1 eq.	P_2O_5.
Magnesia . . .	41·4	2 eq.	2MgO.
Ammonia . . .	34·3	2 eq.	$2H_3N$.
Water . . .	90	10 eq.	10HO.

The mode in which these elements are arranged is unknown. When heated to redness it loses it water and ammonia, and the residue is diphosphate of magnesia, which contains 36·67 per cent. of pure magnesia. At a strong red heat it fuses and appears when cold as a white enamel.

When the materials for forming the preceding salt are mixed while hot, small acicular crystals subside on cooling, which are said by Berzelius to contain less of the two bases than the other salt.

Phosphates of Protoxide of Lead.—The triphosphate is precipitated when acetate of oxide of lead is mixed with a solution of the rhombic phosphate of soda, acetic acid being set free. The triphosphate with basic water is best formed by adding the rhombic phosphate of soda gradually to a hot solution of chloride of lead. The nitrate should not be used for the purpose, as it combines with the precipitate. Both these phosphates are white, and are frequently formed at the same time. The latter fuses readily into a yellow bead, which in cooling acquires crystalline facettes.

Triphosphate of Oxide of Silver.—This compound subsides, of a characteristic yellow colour, when the rhombic phosphate of soda is mixed in solution with nitrate of oxide of silver, nitric acid being set free at the same time. It is apt to retain some of the nitrate in combination. This salt is very soluble in nitric and phosphoric acid, forming the soluble phosphate, and in ammonia. By exposure to light it is speedily blackened; but when protected from this agent, it yields on drying an anhydrous yellow powder, which has a sp. gr. of 7·321 (Stromeyer). Its colour changes on the application of heat to a reddish-brown, but its original tint returns on cooling. It bears a red heat without fusion: at a white heat it fuses, and if kept for some time in a fused state a portion of pyrophosphate is generated.

PYROPHOSPHATES.

The discovery of these salts by Clark has also been mentioned. That modification of phosphoric acid termed *pyrophosphoric acid*, is procured by forcing with the aid of heat phosphoric acid to combine with 2 eq. either of water or some fixed base. The only pyrophosphates which have as yet been studied are those of soda and oxide of silver. These salts are thus constituted:—

Names.	Base.	Acid.	Equiv.	Formulæ.
Dipyrophosphate of Soda . .	62·6	2 eq.+71·4	1 eq.=134·0	$2NaO+P_2O_5$.
Do. in crystals with 90 or 10 eq. of water .			=224	
Acid Dipyrophos. Soda and Basic Water	Soda 31·3 Water 9	1 eq.+71·4	1 eq.=111·7	$NaO,HO+P_2O_5$
Pyrophosphate of Soda . . .	31·3	1 eq.+71·4	1 eq.=102·7	$NaO+P_2O_5$.
Dipyrophos. Oxide of Silver . .	232	2 eq.+71·4	1 eq.=303·4	$2AgO+P_2O_5$.

Dipyrophosphate of Soda.—This is the compound first prepared by Clark from the rhombic phosphate, by expelling its basic water. When the residual mass is dissolved in water and set to evaporate, crystals are obtained, having the outline of an irregular six-sided prism, derived from a rhombic prism. These crystals are permanent in the air, much less soluble in water than the original rhombic phosphate, and quite neutral to test paper. Ignited with carbonate of soda, a phosphate is reproduced, because the acid is forced to unite with 3 eq. of a base.

Dipyrophosphate of soda is permanent both in crystals and in solution in the cold; but by long boiling, or quickly when boiled with an acid, a phosphate is reproduced. With a salt of lead it yields a white dipyrophosphate of oxide of lead; and on washing the precipitate and decomposing by hydrosulphuric acid gas, a solution of pyrophosphoric acid is obtained, which again forms dipyrophosphate of soda when neutralized with soda.

The oxides of most metals of the second class yield with pyrophosphoric acid insoluble or sparingly soluble salts, which may be prepared by double decomposition with dipyrophosphate of soda. It should be held in view, however, as Stromeyer has remarked, that most of these salts are more or less soluble in an excess of dipyrophosphate of soda; and that some of them, such as the dipyrophosphate of the oxides of lead, copper, nickel, cobalt, uranium, bismuth, manganese, and mercury, are dissolved by it with great facility.

Acid Dipyrophosphate of Soda and Water.—This salt is formed by exposing, as stated at page 630, the acid triphosphate to a heat of 400°, when it loses one half of its basic water, and acquires the character of a pyrophosphate. This salt dissolves readily in water, has an acid reaction, and has not been obtained in crystals.

Pyrophosphate of Soda. — When the preceding salt, $NaOHO + P_2O_5$, is heated to 600° or a little higher, it loses its basic water, and yet the acid does not lose the character of pyrophosphoric acid. It is left, therefore, as a simple pyrophosphate of soda, $NaO + P_2O_5$. On adding water part of it dissolves, and part is left as an insoluble white powder. The solution is *quite neutral to test paper;* but on adding nitrate of oxide of silver, the dipyrophosphate of that oxide falls, and free nitric acid remains in solution. The soluble and insoluble pyrophosphate of soda appear identical in composition, and the former at a heat just short of redness may be wholly converted into the latter.

Dipyrophosphate of Oxide of Silver.—This salt is readily formed by double decomposition with dipyrophosphate of soda and nitrate of oxide of silver, the residual liquid being quite neutral to test paper. It falls as a snow-white granular precipitate, which fuses readily at a heat short of incandescence into a dark brown liquid, which becomes a crystalline enamel on cooling.

METAPHOSPHATES.

The only metaphosphates which have yet been examined are those of soda, baryta, and oxide of silver, which are thus constituted:—

Names.		Base.	Acid.	Equiv.	Formulæ.
Metaphosphate of Soda	.	. 31·3 1 eq.	+71·4 1 eq.	=102·7	$NaO+P_2O_5$.
Do.	Baryta	. 76·7 1 eq.	+71·4 1 eq.	=148·1	$BaO+P_2O_5$.
Do.	Ox. Silver	. 116 1 eq.	+71·4 1 eq.	=187·4	$AgO+P_2O_5$.
Submetaphos.	do.	. 348 3 eq.	+142·8 2 eq.	=490·8	$3AgO+2P_2O_5$.

Metaphosphate of Soda.—When the pyrophosphate or acid dipyrophosphate of soda is heated to low redness, it fuses, and on cooling becomes a transparent glass, which deliquesces in a damp air, and is very soluble. The solution has a feeble acid reaction. When mixed with nitrate of oxide of silver, the metaphosphate of that oxide falls in gelatinous flakes, wholly unlike the pyrophosphate, and aggregates together as a soft solid when heated to near 212°. The metaphosphate of soda does not change by keeping, and has not hitherto been made to crystallize. When its solution is evaporated, and kept for some time at 400°, it is reconverted into the acid dipyrophosphate of soda and basic water. All the preceding facts are drawn from Graham's essay. (Phil. Trans. 1833, Part ii.)

Metaphosphate of Baryta falls in gelatinous flakes on adding metaphosphate of soda to a solution of chloride of barium, the latter being in excess as the soda salt dissolves the precipitate. By long-continued boiling metaphosphate of baryta is at length dissolved, and at the same time converted into a phosphate.

The metaphosphate of silver is obtained by precipitation, as above stated. When put, while moist, into boiling water, part of its acid is removed, and the submetaphosphate is generated.

ARSENIATES.

Arsenic acid resembles the phosphoric in composition and in many of its properties, but as far as is yet known is only capable of forming tribasic salts. Those which contain 2 eq. of basic water are, like the phosphates, soluble in water and redden litmus, whence they are commonly considered as bisalts. If only 1 eq. of basic water be present, in which the oxygen of the alkaline base and acid is as 2 to 5, the salt is usually termed a neutral arseniate. When no basic water is present, the salt is usually described as a subarseniate. The two last series of salts, except those with the alkalies, are of sparing solubility in water; but they are dissolved by phosphoric or nitric acid, as well as most acids which do not precipitate the base of the salt.

Many of the arseniates bear a red heat without decomposition, or being otherwise modified in their characters; but they are all decomposed when heated to redness along with charcoal, metallic arsenic being set at liberty. The arseniates of the fixed alkalies and alkaline earths require a rather high temperature for reduction; while the arseniates of the second class of metals, as of lead and copper, are easily reduced in a glass tube by means of a spirit-lamp without danger of melting the glass. Of all the arseniates that of oxide of lead is the most insoluble.

The soluble arseniates are easily recognized by the tests described in the section on arsenic; and the insoluble arseniates, when boiled in a strong solution of the fixed alkaline carbonates, are deprived of their acid, which may then be detected in the usual manner. The free alkali, however, should first be exactly neutralized by pure nitric acid.

The arseniates of lime, and of the oxides of nickel, cobalt, iron, copper, and lead, are natural productions.

The composition of the principal arseniates is contained in the following table:—

Names.	Base.		Acid.	Equiv.	Formulæ.
Triarseniate of Soda .	93·9	3 eq.	+115·4	1 eq.=209·3	$3Na+As_2O_5$.
Do. in crystals with 216 or 24 eq. of water . .				=425·3	
Triarsen. Soda and Basic Water	Soda 62·6 Water 9	2 eq. 1 eq.	+115·4	1 eq.=187	$2NaO,HO+As_2O_5$.
Do. in crystals with 216 or 24 eq. of water . .				=403	
Do. in crystals with 126 or 14 eq. of water . .				=313	
Acid Triarsen. Soda and Basic Water	Soda 31·3 Water 18	1 eq. 2 eq.	+115·4	1 eq.=164·7	$NaO,2HO+As_2O_5$.
Do. in crystals with 18 or 2 eq. of water . .				=182·7	
Triarseniate of Potassa .	141·45	3 eq.	+115·4	1 eq.=256·85	$3KO+As_2O_5$.
Triarsen. of Potassa and Basic Water	Potassa 94·3 Water 9	2 eq. 1 eq.	+115·4	1 eq.=218·7	$2KO,HO+As_2O_5$.
Acid Arsen. of Potas. and Basic Water	Potassa 47·15 Water 18	1 eq. 2 eq.	+115·4	1 eq.=162·55	$KO,2HO+As_2O_5$.

Names.	Base.			Acid.	Equiv.	Formulæ.
Triarseniate of Oxide Am. and Basic Water	Ox.Am. Water	52·30 9	2 eq. 1 eq.	+115·4 1 eq.	=176·7	$2H_4NO,HO+As_2O_5$.
Acid Triarsen. of Ox. Am. and Basic Water	Ox.Am. Water	26·15 18	1 eq. 2 eq.	+115·4 1 eq.	=159·55	$H_4NO,2HO+As_2O_5$.
Triarseniate of Baryta	.	230·1	3 eq.	+115·4 1 eq.	=345·5	$3BaO+As_2O_5$.
Triarseniate do. with Basic Water	Baryta Water	153·4 9	2 eq. 1 eq.	+115·4 1 eq.	=277·8	$2BaO,HO+As_2O_5$.
Acid Triarsen. do. with Basic Water	Baryta Water	76·7 18	1 eq. 2 eq.	+115·4 1 eq.	=210·1	$BaO,2HO+As_2O_5$.
Triarseniate of Lime	.	85·5	3 eq.	+115·4 1 eq.	=200·9	$3CaO+As_2O_5$.
Triarseniate do. and Basic Water	Lime Water	57 9	2 eq. 1 eq.	+115·4 1 eq.	=181·4	$2CaO,Ho+As_2O_5$.
Acid Triarsen. do. and Basic Water	Lime Water	28·5 18	1 eq. 2 eq.	+115·4 1 eq.	=161·9	$CaO,2HO+As_2O_5$.
Triarseniate of Ox. Lead	.	334·8	3 eq.	+115·4 1 eq.	=450·2	$3PbO+As_2O_5$.
Triarseniate do. and Basic Water	Lead Water	223·2 9	2 eq. 1 eq.	+115·4 1 eq.	=347·6	$2PbO,HO+As_2O_5$.
Triarseniate of Ox. Silver	.	348	3 eq.	+115·4 1 eq.	=463·4	$3AgO+As_2O_5$.

Arseniates of Soda.—The triarseniate is made in the same manner as triphosphate of soda, with which it is isomorphous. At 60°, 100 parts of water dissolve 28 of the crystals, and still more by the aid of heat. At 186° they fuse in their water of crystallization.

The triarseniate of soda and basic water corresponds precisely in form and constitution with the corresponding phosphate, and like it parts with its last eq. of water at a red heat; but does not, on losing it, receive any change in its characters. It is efflorescent and alkaline to test paper, and crystallizes best out of an alkaline solution. It is prepared by adding soda or its carbonate in slight excess to a solution of arsenic acid. The salt with 14 eq. of water coincides with the corresponding phosphate.

The acid triarseniate of soda and basic water is prepared like the corresponding phosphate.

The same observation applies to the arseniates of potassa and ammonia, each having its isomorphous arseniate. The triarseniate of potassa crystallizes in needles and with difficulty, like the corresponding triphosphate. The arseniate of potassa may be formed by heating nitre to redness mixed with an equal weight of arsenious acid.

The compound arseniate of potassa and soda agrees in form and composition with the phosphate of those bases.

Arseniates of Baryta.—The triarseniate is best prepared by gradually adding in solution triarseniate of soda to chloride of barium in excess, and falls as a pulverulent heavy precipitate, which is apt to contain a little tiarseniate of baryta and basic water as well as the soda salt, and should therefore be well washed with boiling water. On adding chloride of barium to an excess of triarseniate of soda, the latter salt always falls with the precipitate.

To prepare the triarseniate of baryta and basic water a solution of the rhombic triarseniate of soda is added drop by drop to chloride of barium in solution, when the triarseniate soon appears in white crystalline scales, which contain 3 eq. of water. On reversing the process by adding chloride of barium to the arseniate, the precipitate is a mixture of the triarseniate of baryta, and triarseniate of baryta and water. By the continued action of hot water on the latter, it is partly changed into the acid triarseniate and insoluble triarseniate. The acid triarseniate is obtained by dissolving either of the two former salts, in a moist state, by dilute arsenic acid.

Triarseniates of Lime.—The three salts analogous to those of baryta are obtained by precisely similar processes. The triarseniate of lime and basic water occurs in silky acicular crystals as a rare mineral named *pharmacolite*, which contains 5 eq. of water of crystallization.

Triarseniates of Protoxide of Lead.—The triarseniate is formed by adding in solution acetate of oxide of lead gradually to an excess of triarseniate of soda. The same salt falls when acetate of oxide of lead and the rhombic triarseniate of soda are intermixed, acetic acid being set free. It is a white very insoluble powder, which at a low red heat acquires a yellow tint, which it loses again on cooling.

The triarseniate with basic water may be made by a similar process as for forming the corresponding triphosphate, and is a white insoluble, easily fusible powder.

Triarseniate of Oxide of Silver.—This salt falls as a brick-red powder when nitrate of oxide of silver is mixed in solution with triarseniate of soda or the rhombic triarseniate, in the latter case nitric acid being set free. It is apt to retain some of the nitrate, which cannot be removed by washing; a property which the yellow phosphate of oxide of silver also possesses.

ARSENITES.

These salts have as yet been but little examined. The arsenites of potassa, soda, and ammonia may be prepared by acting with those alkalies on arsenious acid: they are very soluble in water, have an alkaline reaction, and have not been obtained in regular crystals. Most of the other arsenites are insoluble, or sparingly soluble, in pure water; but they are dissolved by an excess of their own acid, with great facility by nitric acid, and by most other acids with which their bases do not form insoluble compounds. The insoluble arsenites are easily formed by double decomposition.

All the arsenites are decomposed when heated in close vessels, the arsenious acid being either dissipated in vapour, or converted, with disengagement of some metallic arsenic, into arseniates. Heated with charcoal or black-flux, the acid is reduced with facility. Formiate of soda answers still better.

The soluble arsenites, if quite neutral, are characterized by forming a yellow arsenite of oxide of silver when mixed with the nitrate of that base, and a green arsenite of protoxide of copper, *Scheele's green*, with sulphate of that oxide. When acidulated with acetic or hydrochloric acid, hydrosulphuric acid causes the formation of orpiment. The insoluble arsenites are all decomposed when boiled in a solution of carbonate of potassa or soda.

The arsenite of potassa is the active principle of Fowler's arsenical solution.

CHROMATES.

The salts of chromic acid are mostly either of a yellow or red colour, the latter tint predominating whenever the acid is in excess. The chromates of oxides of the second class of metals are decomposed by a strong red heat, by which the acid is resolved into the green oxide of chromium and oxygen gas; but the chromates of the fixed alkalies sustain a very high temperature without decomposition. They are all decomposed without exception by the united agency of heat and combustible matter. The neutral chromates of protoxides are similar in constitution to the sulphates, being formed of 1 eq. of the base and 1 of chromic acid, the formula being $MO + CrO_3$.

The chromates are in general sufficiently distinguished by their colour. They may be known chemically by the following character:—On boiling a chromate in hydrochloric acid mixed with alcohol, the chromic acid is at first set free, and is then decomposed, a green solution of the chloride of chromium being generated.

The only native chromate hitherto discovered is the red dichromate of protoxide of lead from Siberia, in the examination of which Vauquelin made the discovery of chromium.

Chromates of Potassa.—The neutral chromate from which all the compounds of chromium are directly or indirectly prepared, is made by heating to redness the native oxide of chromium and iron, commonly called *chromate of iron*, with nitrate of potassa, when chromic acid is generated, and unites with the alkali of the nitre. The object to be held in view is to employ so small a proportion of nitre, that the whole of the alkali may combine with chromic acid, and constitute a neutral chromate, which is easily obtained pure by solution in water and crystallization. For this purpose the chromate of iron is mixed with about a fifth of its weight of nitre, and exposed to a strong heat for a considerable time; and the process is repeated with those portions of the ore which are not attacked in the first operation. It is deposited from its solution in small prismatic anhydrous crystals of a lemon-yellow colour, which, according to Brooke, belong to the right prismatic system.

Chromate of potassa has a cool, bitter, and disagreeable taste. It is soluble to great extent in boiling water, and in twice its weight of that liquid at 60°; but it is insoluble in alcohol. It has an alkaline reaction, and on this account Tassaert[*] regards it as a subsalt; but Thomson has proved that it is neutral in composition, consisting of 52 parts or 1 eq. of chromic acid, and 47·15 parts or 1 eq. of potassa.[†]

Bichromate of potassa, which is made in large quantity at Glasgow for dyeing, is prepared by acidulating the neutral chromate with sulphuric, or still better with acetic acid, and allowing the solution to crystallize by spontaneous evaporation. When slowly formed it is deposited in four-sided tabular crystals, the form of which is an oblique rhombic prism. They have an exceedingly rich red colour, are anhydrous, and consist of 1 eq. of the alkali, and 2 eq. of chromic acid. (Thomson.) They are soluble in about ten times their weight of water at 60°, and the solution reddens litmus paper.

The insoluble salts of chromic acid, such as the chromates of baryta and oxides of zinc, lead, mercury, and silver, are prepared by mixing the soluble salts of those bases with a solution of chromate of potassa. The three former are yellow, the fourth orange-red, and the fifth deep red or purple. The yellow chromate of lead, which consists of 1 eq. of acid and 1 eq. of oxide, is now extensively used as a pigment, and the chromate of oxide of zinc may be used for the same purpose.

A dichromate, composed of 1 eq. of chromic acid and 2 eq. of protoxide of lead, may be formed by boiling the carbonate of that oxide with excess of chromate of potassa. It is of a beautiful red colour, and has been recommended by Badams as a pigment. (An. of Phil. xxv. 303.) It may be also made by boiling the neutral chromate with ammonia or lime-water. Liebig and Wöhler prepare it by fusing nitre at a low red heat, and adding chromate of oxide of lead by degrees until the nitre is nearly exhausted. The chromate of potassa and nitre are then removed by water, and the dichromate is left crystalline in texture, and of so beautiful a tint that it vies with cinnabar. (Pog. An. xxi. 580.)

---

[*] An. de Ch. et Ph. vol. xxii.

[†] Annals of Philosophy, vol. xvi.

Chromates of Silver.—When a soluble salt of chromic acid is added to a solution of nitrate of silver, a deep red-coloured precipitate is obtained, which has usually been considered as the neutral chromate of silver. But it has recently been proved by Warington (Phil. Mag. xi. 489) that if the precipitation be made with acid solutions a bichromate is formed. He also obtained the latter salt by the direct oxidation of metallic silver by a solution of bichromate of potassa acidulated with sulphuric acid. The silver is oxidized at the expense of a part of the chromic acid; while another part, by uniting with the resulting oxide, forms the bichromate, which is deposited in tabular crystals of a rich crimson colour. A chrome alum is at the same time formed, and the oxidation of this silver would appear to be induced by the affinity of the sulphuric acid for the oxide of chromium.

On boiling the bichromate in distilled water, a part is dissolved and separated as the solution cools in beautiful micaceous crystals; but, at the same time, a portion of the salt is decomposed into chromic acid and neutral chromate of silver. As thus formed, the latter is of a dark green colour: it is crimson, however, by transmitted light, and yields by trituration a powder similar in colour to the precipitated chromate.

Bichromate of Chloride of Potassium.—Peligot has described a crystalline compound in which chloride of potassium acts the part of an alkaline base in relation to chromic acid. It is prepared from bichromate of potassa and concentrated hydrochloric acid in the ratio by weight of about 3 to 4, which are to be boiled together for some time in a rather small quantity of water; and it is deposited in flat quadrangular prisms of the same colour as bichromate of potassa.

In this process there is a mutual interchange between the elements of potassa and hydrochloric acid; such that

2 eq. Chromic acid . .	$2CrO_3$	yield	2 eq. Chromic acid . .	$2CrO_3$.
1 eq. Potassa . . .	KO		1 eq. Chlo. of Potassium .	KCl.
1 eq. Hydrochloric acid .	HCl		1 eq. Water . . .	HO.

For this change to ensue there ought to be a certain excess of hydrochloric acid, and yet not so much as to decompose the chromic acid.

This salt should be dried on bibulous paper. It is permanent in the air. In pure water it is decomposed, the materials from which it was formed, bichromate of potassa and hydrochloric acid, being reproduced; but it may be dissolved without such change in water acidulated by hydrochloric acid. Peligot has made similar bichromates with the chlorides of sodium, calcium, and magnesium, and with hydrochlorate of ammonia, this last salt being exactly similar in appearance to the bichromate of chloride of potassium. (An. de Ch. et Ph. lii. 267.)

BORATES.

As the boracic is a feeble acid, it neutralizes alkalies imperfectly, and hence the borates of soda, potassa, and oxide of ammonium have always an alkaline reaction. For the same reason, when the borates are digested in any of the more powerful acids, such as the sulphuric, nitric, or hydrochloric, the boracic acid is separated from its base. This does not happen, however, at high temperatures; for boracic acid, owing to its fixed nature, decomposes at a red heat all salts, not excepting sulphates, the acid of which is volatile.

The borates of the alkalies are soluble in water, but most of the other salts of this acid are of sparing solubility. They are not decomposed by heat, and the alkaline and earthy borates resist the action of heat and combustible matter. They are remarkably fusible in the fire, a property obviously owing to the great fusibility of boracic acid itself.

The borates are distinguished by the following character:—By digesting any borate in a slight excess of strong sulphuric acid, evaporating to dryness, and boiling the residue in strong alcohol, a solution is formed which has the property of burning with a green flame.

Biborate of Soda.— This salt, the only borate of importance, occurs native in some of the lakes of Thibet and Persia, and is extracted from this source by evaporation. It is imported from India in a crude state, under the name of *Tincal*, which, after being purified, constitutes the *refined borax* of commerce. It is frequently called *sub-borate of soda*, a name suggested by the inconsistent and unphilosophical practice, now quite inadmissible, of regulating the nomenclature of salts merely by their action on vegetable colouring matter. It crystallizes in prisms of the oblique system, which effloresce on exposure to the air, and require twenty parts of cold, and six of boiling water, for solution. When exposed to heat, the crystals are first deprived of their water of crystallization, and then fused, forming a vitreous transparent substance called *glass of borax*. The crystals are composed of 69·8 parts or 2 eq. of boracic acid, 31·3 or 1 eq. of soda, and 90 or 10 eq. of water.

The chief use of borax is as a flux, and for the preparation of boracic acid. Biborate of magnesia is a rare natural production, which is known to mineralogists by the name of *Boracite*.

A new biborate of soda, which contains half as much water of crystallization as the preceding, has been lately described by Buran. It is harder and denser than borax, is not efflorescent, and crystallizes in regular octohedrons. It is made by dissolving borax in boiling water until the sp. gr. of the solution is at 30° or 32° of Beaumé's hydrometer: the solution is then very slowly cooled; and when the temperature descends to about 133°, the new salt is deposited. It is found to be more convenient for the use of jewellers than common borax. (An. de Ch. et Ph. xxxvii. 419.)

The neutral borate of soda has been obtained by Berzelius by the action of boracic acid on carbonate of soda at a boiling heat, when carbonic acid is evolved. The solution on cooling yields crystals of the oblique prismatic system, and containing 8 eq. of water. Their constitution is there NaO,BaO_3+8HO. They are powerfully alkaline, and on exposure to the air readily attract carbonic acid, forming the carbonate and biborate of soda. He also obtained the neutral borate of potassa, but was prevented by its great solubility from procuring it in crystals.

CARBONATES.

The carbonates are distinguished from other salts by being decomposed with effervescence, owing to the escape of carbonic acid gas, by nearly all the acids; and all of them, except the carbonates of potassa, soda, and lithia, may be deprived of their acid by heat. The carbonates of baryta and strontia, especially the former, require an intense white heat for decomposition; those of lime and magnesia are reduced to the caustic state by a full red heat; and the other carbonates part with their carbonic acid when heated to dull redness.

All the carbonates, except those of potassa, soda, and ammonia, are of sparing solubility in pure water; but all of them are more or less soluble in an excess of carbonic acid, owing doubtless to the formation of supersalts.

Several of the carbonates occur native, among which may be enumerated the carbonates of soda, baryta, strontia, lime, magnesia, and the protoxides of manganese, iron, copper, and lead; together with some double carbonates, such as dolomite or the double carbonate of lime and magnesia, and baryto-calcite or the double carbonate of baryta and lime.

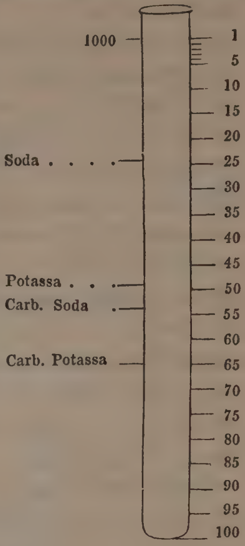
The composition of the principal carbonates is stated in the following table:—

Names.	Base.	Acid.	Equiv.	Formulæ.
Carbonate of Potassa . .	47·15 1 eq.	+22·12 1 eq.	= 69·27	$KO+CO_2$.
Bicarbonate do.	47·15 1 eq.	+44·24 2 eq.	= 91·39	$KO+2CO_2$.
Do. in crystals with 9 or 1 eq. of water . .			=100·39	
Carbonate of Soda	31·3 1 eq.	+22·12 1 eq.	= 53·42	$NaO+CO_2$.
Do. in crystals with 90 or 10 eq. of water .			=143·42	
Do. . . . . . 63 or 7 eq. of water . .			=116·42	
Bicarbonate of Soda . .	31·3 1 eq.	+44·24 2 eq.	= 75·54	$NaO+2CO_2$.
Do. in crystals with 9 or 1 eq. of water . .			= 84·54	
Carbonate of Ammonia .	17·15 1 eq.	+22·12 1 eq.	= 39·27	H_3N+CO_2.
Bicarbonate ditto . .	17·15 1 eq.	+44·24 2 eq.	= 61·39	$H_4NO+2CO_2$.
Carbonate of Baryta . .	76·7 1 eq.	+22·12 1 eq.	= 98·82	$BaO+CO_2$.
—— Strontia . .	51·8 1 eq.	+22·12 1 eq.	= 73·92	$SrO+CO_2$.
—— Lime . .	28·5 1 eq.	+22·12 1 eq.	= 50·62	$CaO+CO_2$.
—— Magnesia .	20·7 1 eq.	+22·12 1 eq.	= 42·82	$MgO+CO_2$.
—— Do. in crystals with 27 or 3 eq. of water .			= 69·82	
Carbonate Protox. of Iron	36 1 eq.	+22·12 1 eq.	= 58·12	$FeO+CO_2$.
Dicarbonate Protox. Copper	79·2 2 eq.	+22·12 1 eq.	=101·32	$2CuO+CO_2$.
Do. in malachite with 9 or 1 eq. of water . . .			=110·32	
Carbonate Protox. Lead	111·6 1 eq.	+22·12 1 eq.	=133·72	
Dicarbon. Perox. Mercury	436 2 eq.	+22·12 1 eq.	=458·12	$2HgO+CO_2$.
Double Carbonates.				
Carbonate of Lime	Carb. Lime . .	50·62 1 eq.	= 93·44	MgO,CO_2+CaO,CO_2.
and Magnesia	Carb. Magnesia .	42·82 1 eq.		
Carbon. of Baryta	Carb. Baryta . .	98·82 1 eq.	=149·44	CaO,CO_2+BaO,CO_2.
and Lime	Carb. Lime . .	50·62 1 eq.		

Carbonate of Potassa.—This salt is procured in an impure form by burning land plants, lixiviating their ashes, and evaporating the solution to dryness; a process which is performed on a large scale in Russia and America. The carbonate, thus obtained, is known in commerce by the names of *potash* and *pearlash*, and is much employed in the arts, especially in the formation of soap and the manufacture of glass. When derived from this source it always contains other compounds, such as sulphate of potassa and chloride of potassium; and therefore, for chemical purposes, it should be prepared from cream of tartar. On heating this salt to redness, the tartaric acid is decomposed, and a pure carbonate of potassa mixed with charcoal remains. The carbonate is then dissolved in water, and, after filtration, is evaporated to dryness in a capsule of platinum or silver.

Pure carbonate of potassa has a taste strongly alkaline, is slightly caustic, and communicates a green tint to the blue colour of the violet. It dissolves in less than an equal weight of water at 60°, deliquesces rapidly on exposure to the air, and crystallizes with much difficulty from its solution. In pure alcohol it is insoluble. It fuses at a full red heat, but undergoes no other change.

It is often necessary, for commercial purposes, to ascertain the value of different samples of pearlash; that is, to determine the quantity of real carbonate of potassa contained in a given weight of impure carbonate. A convenient mode of effecting this object is described by Faraday in his excellent work on *Chemical Manipulation.* Into a tube sealed at one end, $9\frac{1}{2}$ inches long, $\frac{3}{4}$ of an inch in diameter, and as cylindrical as possible in its whole length, pour 1000 grains of water, and with a file or diamond mark the place where its surface reaches, and divide the space occupied by the water into 100 equal parts, as is shown in the annexed woodcut. Opposite to the numbers 23·44, 48·96, 54·63, and 65, draw a line, and at the first write soda, at the second potassa, at the third carbonate of soda, and at the fourth carbonate of potassa. Then prepare a dilute acid having the specific gravity of 1·127 at 60°, which may be made by mixing one measure of concentrated sulphuric acid with four measures of distilled water. This is the standard acid to be used in all the experiments, being of such strength that when poured into the tube till it reaches either of the four marks just mentioned, we shall obtain the exact quantity necessary for neutralizing 100 grains of the alkali written opposite to it. If, when the acid reaches the word *carb. potassa*, and when, consequently, we have the exact quantity which will neutralize 100 grains of that carbonate, pure water be added until it reaches 1, or the beginning of the scale, each division of this mixture will neutralize one grain of carbonate of potassa. All that is now required, in order to ascertain the quantity of real carbonate in any specimen of pearlash, is to dissolve 100 grains of the sample in warm water, filter to remove all the insoluble parts, and add the dilute acid in successive small quantities, until by the test of litmus paper, the solution is exactly neutralized. Each division of the mixture indicates a grain of pure carbonate. It is convenient, in conducting this process, to set aside a portion of the alkaline liquid, in order to neutralize the acid, in case it should at first be added too freely. To this instrument the term *alkalimeter* is given, a name obviously derived from the use to which it is applied.



Bicarbonate of Potassa is made by transmitting a current of carbonic acid gas through a solution of the carbonate; or by evaporating a mixture of the carbonates of ammonia and potassa, the ammonia being dissipated in a pure state. By slow evaporation, the bicarbonate is deposited from the liquid in hydrated prisms with eight sides, terminated with dihedral summits.

Bicarbonate of potassa, though far milder than the carbonate, is alkaline both to the taste and to test paper. It does not deliquesce on exposure to the air. It requires four times its weight of water at 60° for solution, and is much more soluble at 212°; at this temperature it has been stated to be converted into sesquicarbonate, but H. Rose has shown that, though gradually, it at length parts with half its carbonic acid. The escape of the gas he finds to be much retarded by pressure, that of one inch of mercury making a difference; hence the loss of carbonic acid is much more rapid when a cold solution is evaporated in vacuo, both the gas and aqueous vapour being absorbed by quicklime (Pog. An. xxxiv. 149). At a low red heat it is converted into the carbonate.

Thomson, in his "First Principles," has described a sesquicarbonate, which was discovered by Nimmo of Glasgow. Its crystals contain 12 eq. of water, as denoted by the formula $2KO,3CO_2+12HO$.

Carbonate of Soda.—The carbonate of commerce is obtained by lixiviating the ashes of sea-weeds. The best variety is known by the name of *barilla*, and is derived chiefly from the *salsola soda* and *salicornia herbacea.* A very inferior kind, known by the name of *kelp*, is prepared from sea-weeds on the northern shores of Scotland. The purest barilla, however, though well fitted for making soap and glass, and for other purposes in the arts, always contains the sulphates of potassa and soda, and the chlorides of potassium and sodium. A purer carbonate is prepared by heating a mixture of sulphate of soda, saw-dust, and lime, in a reverberatory furnace. By the action of carbonaceous matter, the sulphuric acid is decomposed; its sulphur partly uniting with calcium and partly being dissipated in the form of sulphurous acid, while the carbonic acid, which is generated during the process, unites with soda. The carbonate of soda is then obtained by lixiviation and crystallization. It is difficult to obtain this salt quite free from sulphuric acid.

It crystallizes in rhombic octohedrons, the acute angles of which are generally truncated. The crystals effloresce on exposure to the air, and, when heated, dissolve in their water of crystallization. By continued heat they are rendered anhydrous without loss of carbonic acid. They dissolve in about two parts of cold, and in rather less than their weight of boiling water, and the solution has a strong alkaline taste and reaction. The crystals commonly found in commerce contain 10 eq. of water; but when formed at a temperature of about 80°, they retain only 7 eq.

The purity of different specimens of barilla, or other carbonates of soda, may be obtained by means of the alkalimeter above described.

Bicarbonate of Soda.—This salt is made by the same processes as bicarbonate of potassa, and is deposited in hydrated crystalline grains by evaporation. Though still alkaline, it is much milder than the carbonate, and far less soluble, requiring about ten times its weight of water at 60° for solution. It is found by Rose to undergo the same changes on boiling as the bicarbonate of potassa; it is converted into the carbonate by a red heat.

Sesquicarbonate. — This compound occurs native on the banks of the lakes of soda in the province of Sukena in Africa, whence it is exported under the name of *Trona.* It was first distinguished from the two other carbonates by Phillips (Journal of Science, vii.), whose analysis corresponds with that of Klaproth. Its formula is $2NaO,3CO_2 + 4HO$.

Carbonate of Ammonia.—The only method of obtaining the substance so called is by mixing perfectly dry carbonic acid and ammoniacal gases. In whatever proportion the two gases be mixed, they unite only in the ratio of one volume of the former to two of the latter, and condense into a white light powder. This substance therefore contains carbonic acid and ammonia in equivalent proportions, but it is probable that the elements are not arranged as expressed by the name. By the action of water it is instantly decomposed into ammonia and the sesquicarbonate.

Bircarbonate of Oxide of Ammonium.—This salt was formed by Berthollet by transmitting a current of carbonic acid gas through a solution of the common carbonate of ammonia of the shops. On evaporating the liquid by a gentle heat, the bicarbonate is deposited in small prisms of the right rhombic system, which have no smell, and very little taste. Berthollet ascertained that it contains twice as much acid as the carbonate. It cannot exist without the presence of water, of which it contains 22·7 per cent. (Berzelius), or 2 eq. It may therefore be considered as carbonate of basic water and carbonate of oxide of ammonium, or $HO,CO_2 + H_4NO,CO_2$.

Sesquicarbonate of Oxide of Ammonium.—The common carbonate of ammonia of the shops, *sub-carbonas ammoniæ* of the pharmacopœia, is different from both these compounds. It is prepared by heating a mixture of one part of hydrochlorate of ammonia with one part and a half of carbonate of lime, carefully dried. Double decomposition ensues during the process: chloride of calcium remains in the retort, and hydrated sesquicarbonate of ammonia is sublimed. The carbonic acid and ammonia are, indeed, in proper porportion in the mixture for forming the real carbonate; but, owing to the presence of water generated by the combination of the oxygen of the lime with the hydrogen of the hydrochloric acid, part of the ammonia is disengaged in a free state.

The salt thus formed consists, according to the analysis of Phillips, Ure, and Thomson, of 34·3 parts or 2 eq. of ammonia, 66·36 parts or 3 eq. of carbonic acid, and 18 parts or 2 eq. of water. It is therefore anhydrous sesquicarbonate of oxide of ammonium, or $2H_4NO + 3CO_2$. When recently prepared, it is hard, compact, translucent, of a crystalline texture, and pungent ammoniacal odour; but if exposed to the air, it loses weight rapidly from the escape of pure ammonia, and becomes an opaque brittle mass, which is the bicarbonate. The results obtained by Rose, who has lately studied the carbonates of ammonia with care, will be given in the organic chemistry, where ammonia, as containing a compound radical, is more properly placed.

Carbonate of Baryta occurs abundantly in the lead mines of the north of England, where it was discovered by Dr. Withering, and has hence received the name of *Witherite.* It may be prepared by way of double decomposition, by mixing a soluble salt of baryta with any of the alkaline carbonates or bicarbonates. It is anhydrous, exceedingly insoluble in distilled water, requiring 4300 times its weight of water at 60°, and 2300 of boiling water for solution; but when recently precipitated, it is dissolved much more freely by a solution of carbonic acid. It is highly poisonous.

Carbonate of Strontia, which occurs native at Strontian in Argyleshire, and is known by the name of *Strontianite*, may be prepared in the same manner as carbonate of baryta. It is anhydrous, and very insoluble in pure water, but is dissolved by an excess of carbonic acid.

Carbonate of Lime.—This salt is a very abundant natural production, and occurs under a great variety of forms, such as common limestone, chalk, marble, and Iceland spar, and in regular anhydrous crystals, the density of which is 2·7. It may also be formed by precipitation. Though sparingly soluble in pure water, it is dissolved by carbonic acid in excess; and hence the spring-water of limestone districts always contains carbonate of lime, which is deposited when the water is boiled.

Daniell noticed that an aqueous solution of sugar and lime deposited crystallized carbonate of lime by exposure to the air. Gay-Lussac has proved that the sugar merely acts as a solvent, presenting lime in a favourable state for combining with the carbonic acid of the atmosphere; and that all the lime is deposited in acute rhombohedrons, which contain 5 eq. of water to 1 eq. of carbonate of lime. These crystals are insoluble and remain unchanged in cold water; but in water at 86°, or in air, they lose their combined water, and fall to powder. When boiled in alcohol they retain their form, but lose 2 eq. of water and retain 3 eq. in combination. (An. de Ch. et Ph. xlviii. 301.)

Carbonate of Magnesia.—It is met with occasionally in rhombohedral crystals, and in a pulverulent earthy state, but more commonly as a compact mineral of an earthy fracture called *Magnesite.*

A specimen of magnesite from the East Indies, where, I am informed, it is abundant, has been analyzed by Henry, who found it to be nearly pure anhydrous carbonate of magnesia: it is of a snow-white colour, of density 2·56, and so hard that it strikes fire with steel. (An. of Phil. xvii. 252.) It is obtained in minute transparent hexagonal prisms with 3 eq. of water, when a solution of bicarbonate of magnesia evaporates spontaneously in an open vessel. The crystals lose their water and become opaque by a very gentle heat, and even in a dry air at 60°. By cold water they are decomposed, yielding a soluble bicarbonate and an insoluble white compound of hydrate and carbonate of magnesia; and hot water produces the same change with disengagement of carbonic acid, without dissolving any magnesia. The formula of the crystals is $MgO, CO_2 + 3HO$. (Berzelius.) Fritsche obtained in the same way, besides the salt of Berzelius, another in tabular crystals, containing 5 at. water, $MgO,CO_2 + 5HO$. When heated, it loses carbonic acid, and leaves a new compound, $4(MgO,CO_2) + MgO,5HO$.

When carbonate of potassa is added in excess to a hot solution of sulphate of magnesia, a white precipitate falls, which after being well washed has been long considered as pure carbonate of magnesia; but Berzelius has shown that it consists of the following ingredients:—

Magnesia .	44·75	82·8 or 4 eq.	Probable formula is
Carbonic Acid .	35·77	66·36 or 3 eq.	
Water . .	19·48	36 or 4 eq.	$MgO,4HO+3MgO,CO_2$.
	100·00	185·16 or 1 eq.	

This compound is said to require 2493 parts of cold, and 9000 of hot water for solution. It is freely dissolved by a solution of carbonic acid, bicarbonate of magnesia being generated; but on allowing the solution to evaporate spontaneously, carbonic acid is given off, and crystals of the hydrated carbonate above mentioned are obtained.

Carbonate of Protoxide of Iron.—Carbonic acid does not form a definite compound with peroxide of iron, but with the protoxide it constitutes a salt which is an abundant natural production, occurring sometimes massive, and at other times crystallized in rhombohedrons. This protocarbonate is contained also in most of the chalybeate mineral waters, being held in solution by free carbonic acid; and it may be formed by mixing an alkaline carbonate with the sulphate of protoxide of iron. When prepared by precipitation it attracts oxygen rapidly from the atmosphere, and the protoxide of iron, passing into the state of peroxide, parts with carbonic acid. For this reason, the carbonate of iron of the pharmacopœia is of a red colour, and consists chiefly of the peroxide.

Dicarbonate of Protoxide of Copper.—It occurs as a hydrate in the beautiful green mineral called *malachite*; and the same compound, as a green powder, the *mineral green* of painters, may be obtained by precipitation from a hot solution of sulphate of protoxide of copper by carbonate of soda or potassa. When obtained from a cold solution, it falls as a bulky hydrate of a greenish-blue colour, which contains more water than the green precipitate. By careful drying its water may be expelled. When the hydrate is boiled for a long time in water, it loses both carbonic acid and combined water, and the colour changes to brown. The rust of copper, prepared by exposing metallic copper to air and moisture, is a hydrated dicarbonate.

The blue-coloured mineral, called *blue copper ore*, appears to be a hydrate and carbonate of the protoxide of copper, and consists, according to the analysis of Phillips, of (Quarterly Journal of Science, iv.)

Protoxide of Copper	69·08	118	or 3 eq.	Probable formula is
Carbonic Acid .	25·46	44·24	2 eq.	
Water . .	5·46	9	1 eq.	$CuO,HO+2CuO,CuO_2$.
	100·00	171·24	1 eq.	

The blue pigment called *verditer*, prepared by decomposing nitrate of oxide of copper with chalk, has a similar composition. (Phillips.)

Carbonate of Protoxide of Lead.—This salt, which is the *white lead*, or *ceruse* of painters, occurs native in white prismatic crystals derived from a right rhombic prism, the sp. gravity of which is 6·72. It is obtained as a white pulverulent precipitate by mixing solutions of an alkaline carbonate with acetate of protoxide of lead; and it is prepared as an article of commerce from the subacetate by a current of carbonic acid, by exposing metallic lead in minute division to air and moisture, and by the action on thin sheets of lead of the vapour of vinegar, by which the metal is both oxidized and converted into a carbonate.

Dicarbonate of Peroxide of Mercury.—When a solution of the nitrate of peroxide of mercury is decomposed by carbonate of soda, an ochre-yellow precipitate falls, which Phillips finds to be a dicarbonate. The protoxide appears to form no compound with carbonic acid; for when a nitrate of that oxide is decomposed by any alkaline carbonate, the precipitate is either black at first or speedily becomes so, and after being washed is quite free from carbonic acid.

Double Carbonates.—One of the most remarkable of these is the double carbonate of lime and magnesia, which constitutes the minerals called bitter-spar, pearl-spar, and dolomite. The two former occur in rhombohedrons of nearly the same dimensions as carbonate of lime. The latter is met with in great perfection in the Alps, and there usually occurs in white masses of a granular texture; the grains often cohere loosely, but other specimens are hard and compact, and when broken present the crystalline aspect of marble. Its density is 2·884. Some specimens consist of the two constituent carbonates in the ratio of their eq., as stated in the table; but the ratio of the ingredients, as may be expected, is very variable, since isomorphous substances crystallize together in all proportions. Carbonate of protoxide of manganese is often associated with them. The rock called *magnesian limestone* may be viewed as an impure earthy variety of dolomite.

The double carbonate of baryta and lime constitutes the mineral called *baryto-calcite*, which Mr. Children found to contain the two carbonates in atomic proportion.

Berthier has made some interesting experiments on the production of double carbonates by fusion. Carbonate of soda, when fused with carbonate of baryta, strontia, or lime, in the ratio of their eq., yields uniform crystalline compounds, which have all the appearance of being definite. An eq. of dolomite fuses in like manner with 4 eq. of carbonate of soda. Five parts of carbonate of potassa and four of carbonate of soda, corresponding to an eq. of each, fuse with remarkable facility; and this mixture, by reason of its fusibility, may be advantageously employed in the analysis of earthy minerals.

Compounds similar to the foregoing may be generated by heating sulphate of soda with carbonate of baryta, strontia, or lime, in the ratio of their eq.; or by employing the sulphate of these bases and carbonate of soda. In like manner carbonate of soda fuses with chloride of barium or calcium; and chloride of sodium with carbonate of baryta or lime. (An. de Ch. et Ph. xxxviii.)

SECTION II.

CLASS OF SALTS. ORDER II.

HYDRO-SALTS.

In this section are included those salts only, the acid or base of which is a compound containing hydrogen as one of its elements. For reasons already assigned (page 364-6) I have already described all those salts which were formerly called *muriates* or *hydrochlorates* of metallic oxides as chlorides of metals, considering that in general the neutralizing power of hydrochloric acid is not due to its direct combination with an oxide, but to chlorine uniting with the metal itself. The same remark applies to the hydriodic and other hydracids, the salts of which are consequently reduced to a small number. The only salts, indeed, which are included in this section, are compounds of the hydracids with ammonia and phosphuretted hydrogen. Some of the compounds which might, as containing an hydracid, be comprehended in this section, may with greater propriety be placed in the fourth, seeing that in them the hydracid acts rather as a base or electro-positive ingredient than as an acid or electro-negative substance. This double function, which chemists have long recognized in certain metallic oxides, such as alumina and oxide of zinc, appears to be performed even by so powerful an acid as the hydrochloric. Some judicious observations on this subject have been made by Professor Kane of Dublin. (Dublin Journal of Science, i. 265.)

The compounds of ammonia with the hydracids may be described as chlorides of the hypothetical radical ammonium. The argument for doing so is derived from the similarity of the hydrochlorate of ammonia to the chloride of potassium in its crystalline form, and all its relations to other chlorides. But the argument does not apply with equal force in both cases; for to suppose a direct compound of ammonia and an hydracid is perfectly consistent with observation, whereas the existence of a compound of ammonia and an ox-acid is directly opposed to it. In the former case, therefore, we have two ways of accounting for the phenomena observed; in the latter we have but one, and that one therefore, though hypothetical, must be adopted. As this necessity does not exist in the compounds of ammonia with the hydracids, they are treated as direct binary combinations of their constituents.

Ammonia unites with fluoride of boron, bisulphuret of carbon, and some other bi-elementary compounds, which contain neither oxygen nor hydrogen, constituting saline combinations, which are included in this section, and to which, considering the distinct alkaline character of ammonia, the ordinary nomenclature of salts is applicable.

AMMONIACAL SALTS.

These compounds are readily recognized by the addition of pure potassa or lime, when the odour of ammonia may be perceived. Those which contain a volatile acid may in general be sublimed without decomposition; but the ammonia is expelled by heat from those acids which are much more fixed than itself. The most important of these salts are thus constituted:—

Names.	Base.		Acid.		Equiv.	Formulæ.
Hydrochlorate of Ammonia	17·15	1 eq.+	36·42	1 eq.=	53·57	H_3N+HCl.
Hydriodate do. . .	17·15	1 eq.+	127·3	1 eq.=	144·45	H_3N+HI.
Hydrobromate do. . .	17·15	1 eq.+	79·4	1 eq.=	96·55	H_3N+HBr.
Hydrofluate do. . .	17·15	1 eq.+	19·68	1 eq.=	36·83	H_3N+HF.
Hydrosulphate do. . .	17·15	1 eq.+	17·1	1 eq.=	34·25	H_3N+HS.
Trifluoborate do. . .	51·45	3 eq.+	66·94	1 eq.=	118·39	$3H_3N+BF_3$.
Difluoborate do. . .	34·30	2 eq.+	66·94	1 eq.=	101·24	$2H_3N+BF_3$.
Fluoborate do. . .	17·15	1 eq.+	66·94	1 eq.=	84·09	H_3N+BF_3.
Fluosilicate do. . .	17·15	1 eq.+	78·54	1 eq.=	95·69	H_3N+SiF_3.
Carbosulphate do. . .	17·15	1 eq.+	38·32	1 eq.=	55·47	H_3N+CS_2.

Hydrochlorate of Ammonia.—This salt, *sal-ammoniac* of commerce, was formerly imported from Egypt, where it is procured by sublimation from the soot of camel's dung; but it is now manufactured in Europe by several processes. The most usual is to decompose sulphate of ammonia by the chloride either of sodium or magnesium, when double decomposition ensues, giving rise in both cases to hydrochlorate of ammonia, and to sulphate of soda when chloride of sodium is used, and to sulphate of magnesia when chloride of magnesium is employed. The sal-ammoniac is afterwards obtained in a pure state by sublimation. The method now generally used in this country for obtaining sulphate of oxide of ammonium is, to decompose with sulphuric acid the hydrosulphate and hydrocyanate of ammonia which is collected in the manufacture of coal-gas; but it may also be procured either by lixiviating the soot of coal, which contains sulphate of oxide of ammonium in considerable quantity, or by digesting with gypsum impure sesquicarbonate of oxide of ammonium, procured from the destructive distillation of bones and other mineral substances, so as to form an insoluble carbonate of lime and a soluble sulphate of oxide of ammonium.

Hydrochlorate of ammonia has a pungent saline taste, a density of 1·45, and is tough and difficult to be pulverized. It is soluble in alcohol and water, requiring for solution three times its weight of water at 60°, and an equal weight at 212°. It usually crystallizes from its solution in feathery crystals, but sometimes in cubes or octohedrons. At a temperature below that of ignition it sublimes without fusion or decomposition, and condenses on cool surfaces as an anhydrous salt, which absorbs humidity in a damp atmosphere, but is not deliquescent. It is generated by the direct union of hydrochloric and ammoniacal gases, which unite in equal volumes.

Hydriodate of Ammonia.—It is formed as a white powder by the direct union in equal measures of hydriodic and ammoniacal gases, or by neutralizing a solution of hydriodic acid with ammonia, and evaporating. It crystallizes with difficulty in anhydrous cubes, is very soluble in water, and deliquesces in a moist atmosphere. In close vessels it may be sublimed without change; but it suffers partial decomposition when heated in the open air.

When a concentrated solution of this salt is digested with iodine, a brown solution is obtained, the nature of which is not understood.

Hydrobromate of Ammonia is a white anhydrous salt, which may be formed by similar processes as the hydriodate. It is soluble in water, and crystallizes by evaporation in quadrilateral prisms.

Hydrofluate of Ammonia.—It is prepared by mixing one part of sal-ammoniac with $2\frac{1}{4}$ of fluoride of sodium, both dry and in fine powder, gently heating the mixture in a platinum vessel, and receiving the sublimed salt in a second platinum vessel, the temperature of which is not allowed to exceed 212°. Chloride of sodium is generated, and hydrofluate of ammonia is obtained in small anhydrous prismatic crystals, which may be preserved unchanged in the air, is partly soluble in alcohol, and dissolves readily in water. At an elevated temperature it fuses before subliming. It acts powerfully on glass even in its dry state.

When this salt is introduced in a dry state into ammoniacal gas, absorption ensues, and the resulting salt appears to be a dihydrofluate of ammonia. By sublimation it loses ammonia and becomes neutral. An acid salt, apparently a bi-hydrofluate, is obtained by evaporating the aqueous solution of the neutral hydrofluate, ammonia being disengaged. If the evaporation take place at 100°, it separates in crystalline grains, which redden litmus, and deliquesce rapidly at common temperatures.

Hydrosulphate of Ammonia.—This salt, also called hydrosulphuret of ammonia, and formerly the *Fuming Liquor of Boyle*, is prepared by heating a mixture of one part of sulphur, two of sal-ammoniac, and two of unslaked lime. The changes which ensue have been explained by Gay-Lussac. The volatile products are ammonia and hydrosulphate of ammonia; and the fixed residue consists of sulphate of lime with chloride and sulphuret of calcium. The hydrosulphuric acid is formed from the hydrogen of hydrochloric acid uniting with sulphur, and the oxygen of the sulphuric acid is derived from decomposed lime, the calcium of which is divided between the chlorine of the hydrochloric acid and sulphur. Hydrosulphate of ammonia may also be formed by the direct union of its constituent gases, and if they are mixed in a glass globe kept cool by ice, the salt is deposited in crystals. It is much used as a reagent, and for this purpose is usually prepared by saturating a solution of ammonia with hydrosulphuric acid gas, or by precipitating sulphuret of barium with carbonate of ammonia. A mixture of sulphuret of barium, water, and sal-ammoniac, when distilled, also yields this compound. It is frequently called, by the Continental chemists, sulphuret of ammonium, and has all the characters of a sulphuret.

Fluoborates of Ammonia.— Fluoboric acid combines with three times and with twice its volume of ammoniacal gas, forming a trifluoborate and difluoborate, which are liquid at common temperatures. The neutral fluoborate is formed of equal volumes of its constituent gases, and is a white volatile salt, soluble in water, but which cannot be recovered from the solution; for on evaporation, a subfluoborate of ammonia is expelled, and boracic acid is left in solution. The neutral fluoborate is formed by heating gently either of the subfluoborates.

Fluosilicate of Ammonia.—Fluosilicic acid and ammoniacal gases unite by volume in the ratio of 1 to 2, forming a white volatile salt which is decomposed by water.

Carbosulphate of Ammonia. — When dry ammoniacal gas is brought into contact with bisulphuret of carbon, direct combination ensues, and there results an uncrystalline solid mass of a straw-yellow colour, which may be sublimed without decomposition. By contact with water, or exposure to a moist air, an interchange ensues between the elements of water and bisulphuret of carbon, giving rise to hydrosulphuric and carbonic acids; and a sulphur-salt of an orange-yellow colour, the hydro-carbosulphuret of ammonia, is generated.

Arsenio-persulphate of Ammonia.— Berzelius states that when dry persulphuret of arsenic is exposed to ammoniacal gas, absorption ensues, and a yellowish-white compound results; but the elements are united by a feeble attraction, and on mere exposure to the air, the ammonia escapes.

SALTS OF PHOSPHURETTED HYDROGEN.

Rose has lately called the attention of chemists to the close analogy which exists in the composition of ammonia and phosphuretted hydrogen, and in some of their properties. The latter is a feeble alkaline base, which combines with some of the hydracids. The salt best known is the hydriodate of phosphuretted hydrogen, first noticed by Gay-Lussac, which it formed of 137·3 parts or 1 eq. of acid and 31·4 parts or 1 eq. of base, and crystallizes in cubes. The crystals are permanent while quite dry; but with water, or the moisture of the air, they yield a solution of hydriodic acid, and phosphuretted hydrogen gas escapes. These salts are all decomposed by water, and exist only in the anhydrous state.

SECTION III.

CLASS OF SALTS. ORDER III.

SULPHUR-SALTS.

The compounds described in this section are double sulphurets, just as the oxy-salts in general are double oxides. Their resemblance in composition to salts is perfect. The principal *sulphur-bases* are the protosulphurets of potassium, sodium, lithium, barium, strontium, calcium, and magnesium, and hydro-sulphate of ammonia; and the principal *sulphur-acids* are the sulphurets of arsenic, antimony, tungsten, molybdenum, tellurium, tin, and gold, together with hydrosulphuric acid, bisulphuret of carbon, and sulphuret of selenium. The sulphur-salts with two metals are so constituted, that if the sulphur in each were replaced by an eq. quantity of oxygen, an oxy-salt would result. The analogy between oxy-salts and sulphur-salts is rendered still closer by the circumstance that hydrosulphuric and hydrosulphocyanic acids have the characteristic properties of acidity, and unite both with ammonia and with sulphur-bases.

The sulphur-salts may be divided into families, characterized by containing the same sulphur-acid. For the purpose of indicating that such salts are double sulphurets, as well as to distinguish them readily from other kinds of salts, I shall construct the generic name of each family from the sulphur acid terminated with sulphuret. Thus the salts which contain persulphuret of arsenic or hydrosulphuric acid as the sulphur-acid are termed *arsenio-sulphurets* and *hydro-sulphurets;* and a salt composed of each of these sulphur-acids with sulphuret of potassium is termed *arsenio-sulphuret* and *hydro-sulphuret* of sulphuret of potassium. For the sake of brevity the metal of the base may alone be expressed, it being understood that the positive metal in a sulphur-salt enters as a protosulphuret into the compound.

HYDRO-SULPHURETS.

The sulphur-salts contained in this group have hydrosulphuric acid for their electro-negative ingredient. Most of them which have been studied are soluble in water, and may be obtained in crystals by evaporation. They are decomposed by exposure to the air, yielding at first bisulphurets of the metal, and then a hyposulphite. By acids the hydrosulphuric acid is expelled with effervescence. They are thus constituted :—

Name.	Sulphur-base.	Sulphur-acid.	Equiv.	Formulæ.
Hydro-sulphuret of Potassium	55·25	1 eq.+17·1	1 eq.= 72·35	$KS+HS$.
Ditto Sodium .	40·4	1 eq.+17·1	1 eq.= 57·5	$NaS+HS$.
Ditto Lithium .	26·1	1 eq.+17·1	1 eq.= 43·2	$LS+HS$.
Ditto Barium .	84·8	1 eq.+17·1	1 eq.=10·19	$BaS+HS$.
Ditto Strontium	59·9	1 eq.+17·1	1 eq.= 77·0	$SrS+HS$.
Ditto Calcium .	36·6	1 eq.+17·1	1 eq.= 53·7	$CaS+HS$.
Ditto Magnesium	28·8	1 eq.+17·1	1 eq.= 45·9	$MgS+HS$.

Hydro-sulphuret of Potassium. — This salt is obtained in the anhydrous state by introducing anhydrous carbonate of potassa into a tubulated retort, transmitting through it a current of hydrosulphuric acid gas, and heating the salt to low redness. The mass becomes black, fuses, and boils from the escape of carbonic acid gas and aqueous vapour; and after the ebullition has ceased, the gas is continued to be transmitted, until the retort is quite cold. The resulting anhydrous hydro-sulphuret of potassium, though black while in fusion, is white when cold, and of a crystalline texture; but if air had not been perfectly excluded, it has a yellow tint, owing to the presence of some bisulphuret of potassium.

The same salt is prepared in the moist way by introducing a solution of pure potassa, free from carbonic acid, into a tubulated retort, expelling atmospheric air by a current of hydrogen gas, and then saturating the solution with hydrosulphuric acid. At first the potassa, as in the former process, interchanges elements with the gas, yielding water and protosulphuret of potassium; after which the protosulphuret unites with hydrosulphuric acid. The solution should be evaporated in the retort to the consistence of syrup, a current of hydrogen gas being transmitted through the apparatus the whole time; and on cooling the salt crystallizes in large four or six-sided prisms, which are colourless if air was perfectly excluded. The crystals contain water of crystallization, have an acrid, alkaline, and bitter taste, deliquesce in open vessels, and dissolve freely in water and alcohol. On exposure to the air it acquires a yellow colour, from the formation of bisulphuret of potassium.

Hydro-sulphuret of Sodium.—It is prepared on the same principles as the former salt, and yields by evaporation colourless crystals. When a hot concentrated solution is mixed with a solution of hydrate of soda also concentrated, the mixture on cooling deposits four-sided prisms, which are protosulphuret of sodium with water of crystallization. The interchange of elements is such that

1 eq. Hydro-sulphuret and	1 eq. Soda	yield	2 eq. Sulphuret and	1 eq. water.
$NaS+HS$	NaO		$2NaS$	HO.

Hydro-sulphuret of Lithium may be prepared in the same way as the two former salts, and is left by evaporation as a crystalline solid. When heated in close vessels it parts with its water of crystallization, and like the two former salts retains its acid even at a red heat.

Hydro-sulphuret of Barium.—It is prepared by the action of hydrosulphuric acid on a solution of baryta with the precautions already mentioned for excluding atmospheric air, and crystallizes by evaporation in four-sided prisms, which are very soluble in water, but dissolve sparingly in alcohol. The crystals part with their water of crystallization when heated, and at a commencing red heat give out hydrosulphuric acid, leaving pure sulphuret of barium.

Hydro-sulphuret of Strontium is prepared like the former salt, and crystallizes in large radiated prisms, which when quite dry may be kept several days exposed to the air without change. When heated it loses its water and acid, and protosulphuret of strontium as a white powder is left.

Hydro-sulphuret of Calcium is formed in the same manner as the preceding salts; but it exists only in solution; for on attempting to crystallize by evaporation, hydrosulphuric acid is driven off, and the sulphuret of calcium in prisms of a silky lustre, is deposited. The hydro-sulphuret of magnesium likewise exists only in solution.

CARBO-SULPHURETS.

The acid of these sulphur-salts is bisulphuret of carbon; and the salts themselves are thus constituted:—

Names.	Sulphur.	Sulphur-acid.	Equiv.	Formulæ.
Cabro-sulphuret of Potassium . .	55·25 1 eq.+	38·32 1 eq.=	93·57	$KS+CS_2$.
Ditto Sodium . .	40·4 1 eq.+	38·32 1 eq.=	78·72	$NaS+CS_2$.
Ditto Lithium .	26·1 1 eq.+	38·32 1 eq.=	64·42	$LS+CS_2$.
Ditto Hydrosulphate of Ammonia .	34·25 1 eq.+	38·32 1 eq.=	72·57	$(H_3N+HS)+CS_2$.
Ditto Barium . .	84·8 1 eq.+	38·32 1 eq.=	123·12	$BaS+CS_2$.
Ditto Strontium .	59·9 1 eq.+	38·32 1 eq.=	98·22	$SrS+CS_2$.
Ditto Calcium .	36·6 1 eq.+	38·32 1 eq.=	74·92	$CaS+CS_2$.
Ditto Magnesium .	28·8 1 eq.+	38·32 1 eq.=	67·12	$MgS+CS_2$.

Carbo-sulphuret of Potassium.—On agitating bisulphuret of carbon with a strong alcoholic solution of protosulphuret of potassium, the liquid when set at rest separates into three layers, the lowest of which is carbo-sulphuret of potassium, and is of the consistence of syrup. Another process is to digest bisulphuret of carbon at 86° in a corked bottle full of a strong aqueous solution of protosulphuret of potassium, until the latter is saturated. A concentrated solution of this salt is of a deep orange, almost red, colour; and when evaporated at 86° to the consistence of syrup, a deliquescent yellow crystalline salt is deposited, which is sparingly soluble in alcohol. On heating it to 150° it gives off water of crystallization; and when more strongly heated it is resolved into trisulphuret of potassium and charcoal.

Carbo-sulphuret of Sodium.—It is prepared like the former salt, and separates in yellow crystals from a very concentrated solution. It is deliquescent, and dissolves readily in alcohol as well as water.

The *Carbo-sulphuret of Lithium* resembles the preceding salt, and is very soluble in water and alcohol. Similar carbo-sulphurets are obtained by the action of solutions of sulphuret of barium, strontium, and calcium, on bisulphuret of carbon: the solutions are of an orange colour, and yield crystalline salts by evaporation.

Carbo-sulphuret of Hydrosulphate of Ammonia.—Zeise prepares this salt by filling a bottle with ten measures of nearly absolute alcohol saturated with ammoniacal gas and one measure of bisulphuret of carbon, and inserting a tight cork. As soon as the liquid has acquired a yellowish-brown colour, the bottle is plunged into ice-cold water, when the carbo-sulphuret is deposited either in yellow penniform crystals or as a crystalline powder. The whole is thrown upon a linen filter, and the salt after being washed, first with absolute alcohol and then with ether, is dried by pressure within folds of bibulous paper. This salt is very volatile, passing off entirely at common temperatures, and can only be preserved in well-corked bottles. Exposed to the air it absorbs humidity and acquires a red colour. Its solution may be kept unchanged in bottles filled with it and tightly corked.

The carbo-sulphurets of barium, strontium, and calcium may be obtained by acting on bisulphuret of carbon with a solution of the protosulphurets of those metals. The resulting solutions are of an orange or brown colour, and the salts deposited by evaporation are of a citron-yellow when quite dry. The carbo-sulphuret of barium is of sparing solubility. The carbo-sulphuret of magnesium is best prepared by adding sulphate of magnesia to a solution of carbo-sulphuret of barium. Berzelius has also prepared several carbo-sulphurets of the metals of the second class.

ARSENIO-SULPHURETS.

Berzelius finds that each of the three sulphurets of arsenic is capable of acting as a sulphur-acid, giving rise to three distinct families of sulphur-salts, distinguishable by the terms *arsenio-persulphurets*, *arsenio-sesquisulphurets*, and *arsenio-protosulphurets.*

Persulphuret of arsenic is a very powerful sulphur-acid, violently displacing hydrosulphuric acid from its combinations with sulphur-bases, even at common temperatures; and when digested with earthy or alkaline carbonates, it expels carbonic acid. The salts of this sulphur-acid may be prepared by several different methods:—

1. By digesting the persulphuret of arsenic in a solution of a sulphur-base, such as sulphuret of potassium or sodium, until it is saturated. The resulting soluble arsenio-persulphuret may be employed to prepare insoluble salts of the same sulphur-acid by means of double decomposition. If a persulphuret of potassium is used, sulphur is deposited.

2. By decomposing a hydrosulphuret of a sulphur-base with persulphuret of arsenic, in which case hydrosulphuric gas is disengaged with effervescence.

3. By decomposing a solution of an arseniate by means of hydrosulphuric acid or hydrosulphate of ammonia.

4. By dissolving persulphuret of arsenic in a solution of caustic alkali, such as potassa; when an interchange of elements between portions of the alkali and persulphuret ensues, whereby arsenic acid and protosulphuret of potassium are generated. In this case

1 eq. Persulphuret	& 5 eq. Potassa	yield	1 eq. Arsenic Acid	& 5 eq. Protosulphuret.
As_2S_5	$5KO$		As_2O_5	$5KS$.

Two salts are thus generated and co-exist in the solution, namely, arseniate of potassa and arsenio-sulphuret of potassium. Similar changes invariably occur when sesquisulphuret of arsenic, sesquisulphuret of antimony, and other sulphur-acids are boiled with alkaline solutions: an oxy-salt, the acid of which is formed of oxygen and the electro-negative metal, is always generated; and this salt, if soluble in water, remains together with the sulphur-salt in solution. An alkaline carbonate may be substituted for a pure alkali, but then carbonic acid is expelled. These principles are concerned in the production of kermes, as already explained.

5. The last method which requires mention, is by exposing a mixture of persulphuret of arsenic and an alkaline carbonate to a red heat in a covered vessel. Carbonic acid gas is disengaged; and an interchange of elements, similar to that just explained, takes place between a portion of the alkali and the sulphuret. The fused mass, accordingly, contains an arseniate of the alkali, as well as a sulphur-salt. This tendency to the formation of a double sulphuret is the reason why, in decomposing orpiment by black

flux, the whole of the arsenic is never sublimed: a part is uniformly retained in the form of a sulphur-salt, the arsenio-sesquisulphuret of sulphuret of potassium.

Most of the arsenio-persulphurets of the second class of metals are insoluble; but those of the metals of the alkalies and alkaline earths are very soluble in water, have a lemon-yellow colour in the anhydrous state, and are colourless when combined with water of crystallization or in solution. When exposed to heat in close vessels they give off sulphur, and an arsenio-sesquisulphuret is generated. In the solid state they are very permanent in the air, and even in solution oxidation takes place with great slowness. When decomposed by an acid, persulphuret of arsenic subsides, hydrosulphuric acid gas escapes, and a salt of the alkali is generated. Some chemists may doubt the possibility of the arsenio-persulphurets dissolving as such in water: they may consider the arsenic and the metal of the sulphur-base to be united with oxygen, and all the sulphur with hydrogen; but this supposition, if followed out, leads into such complex and improbable modes of combination, that I see no alternative but implicitly to admit the views here adopted.

The following table exhibits the composition of the principal arsenio-persulphurets:—

Names.	Sulph.-base.	Sulph.-acid.	Equiv.	Formulæ.
Triarse.-persulph. of Potassium .	165·75 3 eq.	+155·9 1 eq.	=321·65	$3KS+As_2S_5$.
Diarse.-persulph. do.	110·5 2 eq.	+155·9 1 eq.	=266·4	$2KS+As_2S_5$.
Arsenio-persulph. do.	55·25 1 eq.	+155·9 1 eq.	=211·15	$KS+As_2S_5$.
Triarse.-persulph. of Sodium . .	121·2 3 eq.	+155·9 1 eq.	=277·1	$3NaS+As_2S_5$.
Do. in crystals with 270 or 30 eq. of water			=547·1	
Diarse.-persulph. of Sodium . .	80·8 2 eq.	+155·9 1 eq.	=236·7	$2NaS+As_2S_5$.
Arsenio-persulph. do.	40·4 1 eq.	+155·9 1 eq.	=196·3	$NaS+As_2S_5$.
Triarse.-persulph. of Hydrosulphate of Ammonia .	102·75 3 eq.	+155·9 1 eq.	=258·65	$3(H_3N+HS)+As_2S_5$.
Diarse.-persulph. do.	68·5 2 eq.	+155·9 1 eq.	=224·4	$2(H_3N+HS)+As_2S_5$.
Arsenio-persulph. do.	34·25 1 eq.	+155·9 1 eq.	=190·15	$(H_3N+HS)+As_2S_5$.

Arsenio-persulphurets of Potassium.—The diarsenio-persulphuret is best obtained by the action of hydrosulphuric acid gas on the diarseniate of potassa, and yields a colourless solution. By evaporation in vacuo it is reduced to a yellowish viscid mass which dries imperfectly, but when exposed for some time to the open air at length becomes a crystalline mass of a lemon-yellow colour, in which rhomboidal tables are perceptible. When this salt is mixed with alcohol, it is resolved into the triarsenio-persulphuret, which is insoluble in the alcohol, and the arsenio-persulphuret, which remains in solution. The latter has not been obtained in the solid state. The former is deliquescent and very soluble in water; but when its solution is gently evaporated, the residue has a radiated crystalline texture.

Arsenio-persulphurets of Sodium.—The diarsenio-persulphuret is formed like the corresponding salt of potassium, is very soluble in water, and by evaporation yields a lemon-yellow mass, which attracts humidity from the air. On mixing its solution with alcohol it is resolved into the arsenio-persulphuret and triarsenio-persulphuret of sodium, and the latter falls in scaly crystals of snowy whiteness, which may be collected on a filter, washed with alcohol, and dried without change. This salt by solution in water and evaporation may be obtained in rhomboidal tables or prisms derived from a rhombic prism. The crystals undergo no change in the air, and contain 30 eq. of water. The arsenio-persulphuret has been obtained only in solution. The *Arsenio-persulphurets of lithium* are very analogous to those of sodium.

Arsenio-persulphurets of hydrosulphate of Ammonia.—The diarsenio-persulphuret is obtained as a colourless solution by decomposing with hydrosulphuric acid gas a solution of triarseniate of oxide of ammonium and basic water. By spontaneous evaporation it becomes a viscid mass of a reddish-yellow colour, and which cannot be fully dried without decomposition. When its solution is mixed with hydrosulphate of ammonia and agitated with hot alcohol, the triarsenio-sulphuret is deposited in colourless prisms, which, after being well washed with alcohol and dried on bibulous paper, undergo no change by exposure to the air. The arsenio-persulphuret remains in the alcoholic solution.

Analogous salts may be similarly prepared with barium, strontium, calcium, and magnesium; and insoluble compounds of the same nature may be formed by way of double decomposition by mixing soluble arsenio-persulphurets with oxy-salts of the second class of metals.

The salts in which sesquisulphuret of arsenic acts as an acid, resemble those of the persulphuret both in their general characters and mode of formation. Those formed with the protosulphuret of arsenic cannot be made in the moist way by direct union of their ingredients; but when solutions of the arsenio-sesquisulphurets are evaporated, spontaneous decomposition takes place, the salts of protosulphuret of arsenic of a reddish-brown colour subside, while arsenio-persulphurets remain in solution.

MOLYBDO-SULPHURETS.

The electro-negative ingredient of these salts is the tersulphuret of molybdenum, and the most remarkable of them is the molybdo-sulphuret of potassium, which is readily formed by decomposing with hydrosulphuric acid gas a rather strong solution of molybdate of potassa. If no iron is present, the liquid acquires a beautiful red colour like the solution of bichromate of potassa, and on evaporation prismatic crystals with four and eight sides are deposited. Berzelius describes this compound as one of the most beautiful which chemistry can produce: the crystals, by transmitted light, are ruby-red, and their surfaces, while moist with the solution which yielded them, shine like the wings of certain insects with a metallic lustre of a rich green tint. The crystals are anhydrous, dissolve readily in water, but are insoluble in alcohol. On the addition of sulphuric or any of the stronger acids, a salt of potassa is generated with escape of hydrosulphuric acid, and precipitation of tersulphuret of molybdenum.

Soluble molybdo-sulphurets of sodium, lithium, and ammonia of a red colour, may be obtained by a process similar to that for preparing the preceding compound. The composition of these salts is as follows:—

Names.	Sulphur-base.	Sulphur acid.	Equiv.	Formulæ.
Molybdo-sulphuret of Potassium	55·25 1 eq.+	96·26 1 eq. =	151·51	$KS+MoS_3$.
Molybdo-sulphuret of Sodium	40·4 1 eq.+	96·26 1 eq. =	136·66	$NaS+MoS_3$.
Molybdo-sulphuret of Lithium	26·1 1 eq.+	96·26 1 eq. =	122·36	$LS+MoS_3$.
Molybdo-sulphuret of Hydrosulphate of Ammonia	34·25 1 eq.+	96·26 1 eq. =	130·51	$(H_3N+HS)+MoS_3$.

Similarly constituted soluble salts of a red or orange colour may be obtained by boiling solutions of sulphuret of barium, strontium, and calcium with an excess of tersulphuret of molybdenum. The insoluble molybdo-sulphurets may be prepared from the former by way of double decomposition.

ANTIMONIO-SULPHURETS.

When two parts of carbonate of potassa are intimately mixed with four of sesquisulphuret of antimony and one part of sulphur, and the mixture is fused, an antimonio-persulphuret of potassium is generated. On digesting in water, a subantimonio-persulphuret is dissolved, and is deposited by gentle evaporation in large colourless tetrahedrons, which become yellow on exposure to the air. The salts which this sulphur-acid forms with other bases have not been examined.

A sulphur-salt of potassium, in which sesquisulphuret of antimony is the acid, remains in solution after the kermes is deposited (page 500), and may be obtained by evaporation in vacuo in colourless irregular crystals which deliquesce rapidly in the air.

TUNGSTO-SULPHURETS.

The best known of these salts is that of potassium, in which tersulphuret of tungsten is combined with protosulphuret of potassium. It is formed when a solution of tungstate of potassa is decomposed by hydrosulphuric acid, and crystallizes by evaporation in flat quadrilateral prisms, which are anhydrous, and are of a pale red colour. It dissolves sparingly in alcohol, but is freely soluble in water, yielding an orange-coloured solution. When mixed with a quantity of acid insufficient for entire decomposition, it forms a bitungsto-sulphuret of a brown colour.

The tungsto-sulphuret of potassium unites with tungstate of potassa as a double salt, which yields a yellow solution, and crystallizes in rectangular tables of a lemon-yellow colour. It combines also with nitrate of potassa, and the resulting double salt crystallizes in large transparent crystals of a ruby-red tint, and when heated detonates like gunpowder.

The tungsto-sulphuret of sodium is prepared from tungstate of soda by hydrosulphuric acid, and crystallizes with difficulty in irregular crystals of a red colour. It deliquesces in the air, and is soluble in water and alcohol.

SECTION IV.

CLASS OF SALTS. ORDER IV.

HALOID-SALTS.

In this section are included substances composed like the preceding salts of two bi-elementary compounds, one or both of which are analogous in composition to sea-salt. The principal groups consist of double chlorides, double iodides, and double fluorides. In these the haloid-bases belong usually to the electro-positive metals, and the haloid-acids to the metals which are electro-negative. I shall apply to them the same principle of nomenclature as to the sulphur-salts.

HYDRARGO-CHLORIDES.

The haloid-acid of this family is bichloride of mercury, which reddens litmus paper, and loses the property when a haloid-base is present, thus bearing a close analogy to ordinary acids. Its principal salts which have been examined are thus constituted :—

Names.	Basic Chloride.	Bichlor.	Merc.	Equiv.	Formulæ.
Dihydrargo-chloride of Potassium . .	149·14	2 eq.+273·84	1 eq.	=422·98	$2KCl+HgCl_2$.
Do. in rhombic prisms with 18 or 2 eq. of water				=440·98	
Hydrargo-chloride of Potassium . .	74·57	1 eq.+273·84	1 eq.	=348·41	$KCl+HgCl_2$.
Do. in acicular crystals with 18 or 2 eq. of water				=366·41	
Bihydrargo-chloride of Potassium . .	74·57	1 eq.+547·68	2 eq.	=622·25	$KCl+2HgCl_2$.
Do. in acicular crystals with 36 or 4 eq. of water				=658·25	
Hydrargo-chloride of Sodium . . .	59·72	1 eq.+273·84	1 eq.	=333·56	$NaCl+HgCl_2$.
Do. in crystals with 36 or 4 eq. of water . .				=369·56	
Dihydrargo-chloride of hydrochlo. of Ammonia	105·14	1 eq.+273·84	1 eq.	=378·98	$2(H_3N+HCl)$ $+HgCl_2$.
Do. in flat rhombic prisms with 18 or 2 eq. of water				=396·98	

The preceding salts, except the last, were first prepared and examined by Bonsdorff (An. de Ch. et Ph. xliv. 189); and they are obtained by mixing the ingredients in the ratio for combining, and setting aside the solution to crystallize. The ammoniacal salt has long been known under the name of *salt of alembroth*. Bonsdorff obtained similar compounds with the chlorides of lithium, barium, strontium, calcium, magnesium, manganese, iron, cobalt, nickel, and copper. Those of lithium, calcium, magnesium, and zinc are deliquescent. The hydrargo-chlorides of iron and manganese are isomorphous, and crystallize in rhombic prisms. Hydrochloric acid combines with bichloride of mercury, and yields a very soluble salt, which may be obtained in crystals: the electro-positive ingredient is here probably hydrochloric acid, and as such will be considered as chloride of hydrogen, with properties analogous to the chlorides of electro-positive metals.

AURO-CHLORIDES.

These salts, the electro-negative ingredient of which is the terchloride of gold, have been studied by Berzelius, Johnston, and Bonsdorff. They are prepared by mixing the chlorides in atomic proportions, and setting aside the solution to crystallize.

Most of them have an orange or yellow colour, and consist of single equivalents of their constituent chlorides, as is exemplified by the composition of the three following salts :—

Names.	Basic Chlorides.	Terch. Gold.	Equiv.	Formulæ.
Auro-chloride of Potassium . . .	74·57 1 eq.+	305·46 1 eq.	=380·03	$KCl+AuCl_3$.
Do. in prisms with 45 or 5 eq. of water .			=425·03	
Auro-chloride of Sodium	59·72 1 eq.+	305·46 1 eq.	=365·18	$NaCl+AuCl_3$.
Do. in 4-sided prisms with 36 or 4 eq. of water			=401·18	
Auro-chloride of hydrochlorate of Ammonia	105·14 1 eq.+	305·46 1 eq.	=410·60	(H_3N+HCl) $AuCl_3$.
Do. in acicular crystals with 36 or 4 eq. of water			=446·6	

Auro-chloride of Potassium.—This salt crystallizes either in striated prisms or thin hexagonal tables, which effloresce in a dry air, and lose all their water at 212°. At a red heat, the terchloride of gold is decomposed, leaving chloride of potassium and metallic gold. This salt is soluble both in water and alcohol.

Auro-chloride of Sodium crystallizes in long quadrilateral prisms, which may be exposed to the air without change, and fuse readily in their water of crystallization. The *auro-chloride of lithium* is deliquescent.

Auro-chloride of Hydrochlorate of Ammonia.—It crystallizes in transparent needles or small prisms, which become opaque by exposure to the air, and are soluble in water and alcohol.

Auro-chloride of Hydrogen.—In this compound hydrochloric acid is probably the positive chloride. It crystallizes readily in long acicular crystals of a light yellow colour when an acid solution of gold is cautiously evaporated. The crystals undergo no change in dry air, but in a moist atmosphere deliquesce into a yellow liquid.

Bonsdorff has prepared the auro-chlorides of barium, strontium, calcium, magnesium, manganese, zinc, cadmium, cobalt, and nickel. Most of them crystallize in prisms and contain water of crystallization.

PLATINO-CHLORIDES.

Both the protochloride and bichloride of platinum act as haloid-acids. Magnus prepared the platino-protochloride of potassium by mixing chloride of potassium with a solution of protochloride of platinum in hydrochloric acid. It crystallizes by evaporation in red, anhydrous, 4-sided prisms, which are insoluble in alcohol, but dissolve readily in water. It consists of single equivalents of its constituent chlorides.

The *platino-protochloride of sodium* may also be prepared, is soluble in water and alcohol, and crystallizes with difficulty. A similar salt may be formed with hydrochlorate of ammonia, and is isomorphous with that of potassium, which it also resembles in its properties, composition, and mode of preparation.

The solution of protochloride of platinum in hydrochloric acid, which has a deep red tint, is doubtless a double chloride, but it has not been obtained in crystals.

The principal salts of bichloride of platinum are those of potassium, sodium, and ammonia, which are thus constituted :—

Names.	Basic Chlorides.	Bichl. of Plat.	Equiv.	Formulæ.
Platino-bichloride of Potassium . .	74·57 1 eq.	+169·64 1 eq.	=244·21	$KCl+PlCl_2$.
———— Sodium	59·72 1 eq.	+169·64 1 eq.	=229·36	$NaCl+PlCl_2$.
Do. in prisms with 54 or 6 eq. of water . .			=283·36	
Platino-bichloride of hydrochlorate of Ammonia	105·14 1 eq.	+169·64 1 eq.	=274·78	(H_3N+HCl) $+PlCl_2$.

Platino-bichloride of Potassium.—The production of this salt by mixing its constituents in solution, constitutes one of the best tests for potassa. It is commonly obtained as a powder, of a pale lemon-yellow colour; but by slow evaporation it yields small octohedrons of a brilliant lustre. It is anhydrous, insoluble in alcohol, and is sparingly dissolved by cold, but more freely by hot water.

Heated to redness it yields chlorine, and the residue consists of platinum and chloride of potassium.

Platino-bichloride of Sodium.—This salt crystallizes in fine transparent prisms of a deep yellow colour, which are soluble in water and alcohol. When gently heated it loses its water of crystallization, and becomes a pale yellow powder.

Platino-bichloride of Hydrochlorate of Ammonia falls as a lemon-yellow powder when sal-ammoniac is mixed with a strong solution of bichloride of platinum. It resembles the double salt of potassium in its properties and form, crystallizing in small anhydrous octohedrons when its aqueous solution is slowly evaporated. This salt is employed in the preparation of platinum, and when heated to redness leaves that metal in a spongy state.

Bonsdorff has prepared the platino-bichlorides of barium, strontium, calcium, and several other metals. Most of them crystallize with water of crystallization, and have a yellow or orange colour.

PALLADIO-CHLORIDES.

Both of the chlorides of palladium act as haloid-acids, combining with many of the metallic chlorides, when their respective solutions are mixed and evaporated. The principal ones which have been examined are those with potassium, sodium, and ammonia, which consist of single equivalents of their ingredients.

The palladio-protochloride of potassium crystallizes in four-sided prisms of a dirty yellow colour, which are anhydrous, insoluble in alcohol, and freely soluble in water. The corresponding salt of sodium is deliquescent and soluble both in water and alcohol. That of hydrochlorate of ammonia is isomorphous with the salt of potassium, which it resembles in its other properties.

The palladio-bichloride of potassium is obtained by evaporating the palladio-protochloride with nitro-hydrochloric acid, when microscopic crystals of a cinnabar-red colour are deposited, which by a glass are found to be regular octohedrons. It is anhydrous, insoluble in alcohol, and nearly so in water. When heated, or by continued ebullition, it is reconverted into the palladio-protochloride of potassium. The corresponding salt of hydrochlorate of ammonia is obtained in a similar manner, and resembles the former in form and other properties.

RHODIO-CHLORIDES.

The sesquichloride of rhodium combines with the chlorides of potassium and sodium, and the resulting salts are thus constituted :—

Names.	Basic Chlor.	Sesquichl. Rhod.	Equiv.	Formulæ.
Dirhodio-chloride of Potassium	149·14 2 eq.+	210·66 1 eq.	=359·80	$2KCl+R_2Cl_3$.
Do. in four-sided prisms with 18 or 2 eq. of water			=377·8	
Trirhodio-chloride of Sodium	179·16 3 eq.+	210·66 1 eq.	=389·82	$3NaCl+R_2Cl_3$.
Do. in prisms with 162 or 18 eq. of water			=551·82.	

Dirhodio-chloride of Potassium.—It is obtained by mixing the respective chlorides in the ratio above assigned, and crystallizes in four-sided rectangular prisms, which are of a deep red colour, insoluble in alcohol, and contain 18 parts or 2 eq. of water combined with 359·8 parts or 1 eq. of the salt.

Hydrochlorate of ammonia yields a similar double salt, analogous in its properties to the preceding.

Trirhodio-chloride of Sodium.—This salt crystallizes in large prismatic crystals of a deep red colour, which lose part of their water in a dry air, and become covered with a red powder. They are insoluble in alcohol.

IRIDIO-CHLORIDES.

The chlorides of iridium act as haloid-acids. The most remarkable of its salts is the iridio-bichloride of potassium, which in form and properties resembles the platino-bichloride of potassium, crystallizing in brilliant octohedrons, but of a black colour, which are sparingly soluble in water. Hydrochlorate of ammonia forms with it a similar salt, which is of a deep cherry-red colour.

OSMIO-CHLORIDES.

Berzelius has described the osmio-bichloride of potassium, which resembles in form, composition, and most of its properties, the corresponding salts of platinium and iridium. It is insoluble in alcohol, and but sparingly dissolved in water; but its aqueous solution, when gently evaporated, yields octohedral crystals of a deep brown colour.

OXY-CHLORIDES.

Chemists are acquainted with a considerable number of compounds in which a metallic oxide is united with a chloride either of the same metal, which is the most frequent, or of some other chloride. These compounds are commonly termed *sub-muriates*, on the supposition that they consist of hydrochloric acid combined with two or more eq. of an oxide.

Oxy-chlorides of Iron.—When the crystallized protochloride of iron is heated without exposure to the air, the last portions of its water exchange elements with part of the chloride of iron, yielding hydrochloric acid, which is evolved, and protoxide of iron. On raising the heat so as to expel the pure chloride of iron, a deep green oxy-chloride in scaly crystals remains. (Berzelius.)

The ochreous matter which falls when a solution of the protochloride of iron is exposed to the air, is hydrated peroxide of iron combined with some perchloride. A similar hydrate is obtained by mixing with a solution of the perchloride of iron a quantity of alkali insufficient for complete decomposition. When a solution of the perchloride is evaporated to dryness without exposure to the air, the last portions of water exchange elements with the perchloride, hydrochloric acid is disengaged, and after subliming the pure anhydrous perchloride, a compound in large, brown, shining laminæ is left, which consists of peroxide and perchloride of iron. (Berzelius.)

Mr. Phillips has described a soluble oxy-chloride which appears to consist of 1 eq. of perchloride of iron with 9 eq. of the peroxide. It is prepared by digesting hydrochloric acid with the required proportion of the moist hydrated peroxide. The solution is of a brownish-red colour, and a precipitate is occasioned either by a little more of the peroxide or a little acid, indicating the formation of other oxy-chlorides which are insoluble. (Phil. Mag. and An. viii. 406.)

By adding bleaching-liquor to protonitrate of iron, Millon obtained an oxychloride, corresponding to the sesquioxide, which it resembles in appearance. Its formula is $Fe_2\left.\begin{matrix}O_2\\Cl\end{matrix}\right\}$.

Oxy-chlorides of Tin.—When a large quantity of water is poured on crystallized protochloride of tin, a portion of water and protochloride exchange elements, an acid solution is formed, containing the double chloride of tin and hydrogen, and a white powder subsides, which is a compound of the protoxide and protochloride of tin.

Oxy-chloride of Chromium.—This compound, which was long considered as the terchloride, was first shown to be an oxy-chloride by Rose. It has already been mentioned at page 474.

Oxy-chloride of Tungsten.—This compound, the nature of which was first pointed out by Rose, has already been described at page 490.

Oxy-chloride of Molybdenum.—Formerly described as the terchloride, but shown by Rose to be really similar in constitution to the two preceding compounds (page 486).

Oxy-chloride of Antimony.—It falls as a white curdy precipitate when sesquichloride of antimony is thrown into water (page 499), and, according to an analysis by Phillips, contains about 7·8 per cent. of chlorine.

Oxy-chloride of Cerium.—This compound is generated by heating the hydrated protochloride, just as when the protochloride of iron is distilled.

Oxy-chloride of Bismuth.—It is prepared by pouring a neutral solution of nitrate of oxide of bismuth into a concentrated solution of sea-salt; and a similar compound, but with more oxide, is formed when a dilute solution of sea-salt is used. They are both heavy insoluble powders of a very white colour.

Oxy-chloride of Copper.—This compound falls as a green hydrate when potassa is added to a solution of chloride of copper in quantity insufficient for its complete decomposition. When its water is expelled it becomes of a liver-brown colour. Berzelius states it to consist of 1 eq. of the chloride and 3 eq. of oxide of copper. It is used as a pigment under the name of *Brunswick green*, being prepared for that purpose by exposing metallic copper to hydrochloric acid or a solution of sal-ammoniac. The same compound is generated during the corrosion of copper in sea-water. Millon, by the process above mentioned, obtained an oxy-chloride of copper, $Cu_2{\begin{matrix}O\\Cl\end{matrix}}\Big\}$, which seems to be a basic compound.

Oxy-chlorides of Lead.—A compound of 1 eq. protochloride to 2 eq. of protoxide of lead has been found as a colourless mineral. Another oxy-chloride with 3 eq. of the protoxide is prepared by adding pure ammonia to a hot solution of chloride of lead. It falls as a heavy white hydrate; but on expelling its water by heat, it acquires a pale yellow colour. A third oxy-chloride with a still larger proportion of oxide is used as a pigment under the name of *mineral* or *patent yellow ;* and it is prepared by the action of moist sea-salt on litharge, by which means portions of the protoxide and sea-salt exchange elements, yielding soda and chloride of lead. After washing away the alkali, the mixed oxide and chloride are dried and fused. Millon states that bleaching liquor, added to nitrate of lead, throws down a white precipitate, which soon becomes brown. These colours indicate different mechanical states of the same compound, $\mathrm{Pb}\left.\begin{matrix}\mathrm{O}\\\mathrm{Cl}\end{matrix}\right\}$; that is an oxychloride, corresponding to the peroxide, $\mathrm{Pb}\left.\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}\right\}$.

Oxy-chloride of Mercury.—This compound is obtained as a shining crystalline powder, of a brownish-black colour, when peroxide of mercury is boiled with a solution of the bichloride. It is anhydrous, and consists of single equivalents of the oxide and chloride. Formula, $\mathrm{HgO_2 + HgCl_2}$ or $\mathrm{Hg}\left.\begin{matrix}\mathrm{O}\\\mathrm{Cl}\end{matrix}\right\}$.

Millon's experiments alluded to above, and in the section on the hypochlorites, if confirmed, will add the bleaching compounds to the order of oxy-chlorides; and render it probable that oxy-chlorides in general are not compounds of oxides and chlorides, but compounds of the metal with oxygen and chlorine corresponding to the peroxides of the respective metals.

CHLORIDES WITH AMMONIA.

Several interesting compounds of chlorides with ammonia have been studied by Persoz and Rose. (An. de Ch. et Ph. xliv. 315. and li. 5, and Pog. Annalen, xx. 149.) The perchlorides of tin, titanium, antimony and iron, and the oxy-chloride of chromium, absorb ammonia at common temperatures; and most of the other chlorides absorb it when gently warmed. The chlorides of potassium, sodium, and barium do not absorb ammonia; while those of strontium and calcium combine with 4 eq. of the alkali. Chloride of copper absorbs 3 eq. and acquires the same deep blue tint as the ammoniaco-sulphate of copper. Chloride of nickel unites with 3, and chloride of cobalt with 2 eq. of ammonia. Chloride of silver takes up slowly $1\frac{1}{2}$ eq. Calomel absorbs half an eq. and forms a black compound; but on exposure to the air the ammonia flies off, and pure white calomel remains. Corrosive sublimate, by the aid of heat, rapidly absorbs half an eq. of ammonia, and forms a white compound, which is insoluble in water, and bears a considerable temperature without decomposition: the white precipitate of pharmacy is probably analogous in nature, though the ratio of its ingredients is different. Perchloride of titanium combines with 2 eq. and that of tin with 1. The bromides and iodides, as well as the bicyanuret of mercury, absorb ammonia in the same manner as the chlorides. Nearly all of these compounds depend on very feeble affinities. Most of them lose their ammonia by mere exposure to the air, and it is expelled from nearly all by a very moderate heat: in some, as with perchloride of titanium, heat occasions reactions between the chlorine and ammonia, and the metal is insulated; but in general the alkali is simply expelled, and the chloride returns to its former condition. Though these ammoniacal chlorides may be viewed as salts in which a metallic chloride acts as an acid, they appear to be more closely allied to those singular compounds of ammonia with the oxy-salts which have already been noticed. To this remark some of them, of which the ammoniacal chloride of mercury is an instance, are probably exceptions, and are rather, as Kane has shown, to be viewed as compounds of amide. They will be referred to in this form in the organic chemistry.

CHLORIDES WITH PHOSPHURETTED HYDROGEN.

The analogy which Rose has traced between ammonia and phosphuretted hydrogen is especially remarkable in the compounds which they both form with metallic chlorides. He has examined the compounds of phosphuretted hydrogen with the perchlorides of titanium, tin, antimony, iron, and alumina, all of which correspond to ammoniacal chlorides of similar composition. The phosphuretted hydrogen is in all readily displaced by water, or a solution of ammonia. Rose observed that the resulting compound is the same in character and composition whichever of the two kinds of phosphuretted hydrogen were used in its preparation. He also found that the gas, when displaced from perchloride of titanium by water, does not inflame spontaneously; whereas, if displaced by a solution of potassa or its carbonate, by carbonate of ammonia or hydrochloric acid, the gas is spontaneously inflammable. He was thus able to disengage at will either variety of phosphuretted hydrogen from the same compound, without reference to the kind which had been used in its preparation. These facts first led Rose to the opinion that the two gases of phosphorus and hydrogen must be identical in composition.

DOUBLE IODIDES.

These compounds have not yet been closely studied; but there is no doubt that the iodides are capable of forming with each other an extensive series of compounds. Bonsdorff obtained the hydrargo-biniodide of potassium by saturating a strong solution of iodide of potassium with biniodide of mercury: it may also be formed by dissolving corrosive sublimate in a solution of iodide of potassium, evaporating to dryness, and digesting in alcohol, when the double iodide is dissolved, and chloride of potassium is left. A variety of double iodides have been described by Boullay, and among them a compound of biniodide of mercury and hydriodic acid. (An. de Ch. et Ph. xxxiv.) In general the double hydrargo-biniodides contain single equivalents of the respective iodides. Liebig obtained a compound of the bichloride and biniodide of mercury, consisting of 2 eq. of the former to 1 eq. of the latter, as indicated by the formula $HgI_2 + 2HgCl_2$.

Several compounds of biniodide of platinum with other iodides have been studied by Kane and Lassaigne. (Dublin Journal of Science, i. 304, and An. de Ch. et Ph. li. 125.) The compounds at present known are thus constituted:—

Names.	Basic Iod.	Biniod. Plat.	Equiv.	Formulæ.
Platino-biniodide of Potassium	165·45 1 eq.	+351·4 1 eq.	=516·85	$KI+Pt\,I_2$.
Do. of Sodium .	150·6 1 eq.	+351·4 1 eq.	=502·0	$NaI+Pt\,I_2$.
Do. of Hydriodate of Ammonia	144·45 1 eq.	+351·4 1 eq.	=495·85	$NH_4I+Pt\,I_2$.
Do. of Barium .	195 1 eq.	+351·4 1 eq.	=546·4	$BaI+Pt\,I_2$.
Do. of Zinc :	158·6 1 eq.	+351·4 1 eq.	=510·0	$ZnI+Pt\,I_2$.
Do. of Hydrogen	127·3 1 eq.	+351·4 1 eq.	=478·7	$HI+Pt\,I_2$.

The platino-biniodide of potassium is prepared by digesting an excess of biniodide of platinum in a rather concentrated solution of iodide of potassium. By spontaneous evaporation it crystallizes in small rectangular plates surmounted sometimes with a four-sided pyramid, which are anhydrous, unchanged in the air, and insoluble in alcohol. The colour of the crystals is black with a metallic lustre, and they yield a deep claret-coloured solution with water.

The biniodide of platinum appears to combine also with the iodide of platinum; but the compound has only been obtained in solution.

The platino-biniodides of sodium, barium, and zinc are obtained in the same manner as that of potassium, crystallize with difficulty, are deliquescent in the air, and dissolve in water and alcohol. The ammoniacal salt is analogous in its properties to that of potassium, with which it appears also to be isomorphous.

Platino-biniodide of Hydrogen.—This compound consists of hydriodic acid and biniodide of platinum, in which the former is regarded as the electro-positive element. It is prepared by acting on biniodide of platinum with a cold dilute solution of hydriodic acid, which gradually acquires a deep claret colour, and by evaporation under a bell-jar with quicklime, deposits black acicular crystals. The crystals become moist by exposure to the air.

Oxy-iodides.— The principal oxy-iodides at present known to chemists are those formed by the oxide and iodide of lead. When iodide of potassium is mixed with acetate of oxide of lead in excess, the yellow chloride at first formed combines with oxide of lead and acquires a white colour; and the same compound is obtained directly by employing a subacetate. Denot finds that there are three oxy-iodides, in which 1 eq. of iodide of lead is united with 1, 2, and 5 eq. of oxide of lead.

DOUBLE BROMIDES.

These compounds have not yet been studied; but Bonsdorff has proved the possibility of forming compounds similar in composition and properties to the double chlorides. He obtained the hydrargo-bibromide of potassium in crystals, consisting of 1 eq. of each bromide united with 2 eq. of water.

DOUBLE FLUORIDES.

The researches of Berzelius have led to the formation of several extensive families of double fluorides, in which the fluorides of boron, silicon, titanium, and of other electro-negative metals are the acids, and the fluorides of electro-positive metals are bases. In some instances hydrofluoric acid is a haloid-acid; but more commonly it acts the part of a base.

Hydro-fluorides.—In this family hydrofluoric acid is combined with the fluorides of electro-positive metals. If an equivalent of any electro-positive metal be indicated by M, then the general formula for this family is $MF + HF$.

The hydro-fluoride of potassium is made by mixing hydrofluoric acid with a solution of fluoride of potassium, and evaporating by a gentle heat in a platinum capsule. It commonly crystallizes in confused laminæ; but by slow evaporation in square tables or cubes, which are anhydrous and dissolve freely in pure water. It fuses readily when heated, and loses all its hydrofluoric acid at a low red heat.

The hydro-fluoride of sodium is prepared as the preceding salt, and by spontaneous evaporation yields anhydrous rhombohedral crystals. It is sparingly soluble in cold, but much more freely in hot water. The hydro-fluoride of lithium is also of sparing solubility. The fluorides of barium, strontium, calcium, and magnesium do not combine with hydrofluoric acid.

BORO-FLUORIDES.

When the terfluoride of boron (fluoboric acid gas) is acted upon by water, one out of every four eq. of the gas interchanges elements with water, giving rise to hydrofluoric and boracic acids, the former of which combines as a haloid-base with undecomposed terfluoride of boron, constituting the boro-hydrofluoric acid, but which may be viewed as the *boro-fluoride of hydrogen*. This change is such that

4 eq. Terfluoride of Boron	$4BF_3$	yield	3 eq. Terfluoride of Boron .	$3BF_3$.
			3 eq. Hydrofluoric Acid .	$3HF$.
and 3 eq. of water . .	$3HO$		and 1 eq. Boracic Acid .	BO_3.

By careful concentration and cooling, the boracic acid separates as a crystalline powder, and the boro-fluoride of hydrogen remains in solution. It is strongly acid to test paper, and its composition is indicated by the formula $HF + BF_3$, being an eq. of each fluoride. On adding potassa to this compound, it interchanges elements with hydrofluoric acid, and there results the boro-fluoride of potassium, $KF + BF_3$, the hydrogen being simply displaced by potassium. The protoxides of most other metals act precisely like potassa, and therefore the general formula of these compounds is $MF + BF_3$. When exposed to a strong heat, they all give off terfluoride of boron, and a metallic fluoride is left.

Boro-fluoride of Potassium.—It is prepared by dropping boro-fluoride of hydrogen drop by drop into a solution of a salt of potassa, and falls as a gelatinous transparent hydrate, which is a white very fine powder when dried. It has a slightly bitter taste, and is quite neutral to test paper, is very sparingly soluble in alcohol and cold water, but is dissolved freely by hot water, and subsides on cooling in small brilliant anhydrous crystals. At a strong red heat it gives off the terfluoride of boron, and fluoride of potassium remains.

The *boro-fluoride of sodium* is very soluble in water, and is therefore best obtained by the direct action of boro-fluoride of hydrogen on fluoride of sodium. It crystallizes by slow evaporation in large rectangular prisms, which redden litmus paper strongly. The boro-fluoride of lithium also crystallizes in large prisms, is very soluble in water, and deliquesces in the air.

The *boro-fluoride of barium* is prepared by adding carbonate of baryta to boro-fluoride of hydrogen till it ceases to be dissolved, avoiding any further addition. On evaporating to the consistence of a syrup long acicular crystals form, and by keeping the solution in a warm place it yields flat, four-sided, rectangular prisms. It is acid to test paper, and deliquescent. The boro-fluorides of calcium and magnesium may be prepared in a similar manner, and are soluble in water. Lead forms a soluble boro-fluoride, which crystallizes in the same manner as the boro-fluoride of barium.

SILICO-FLUORIDES.

The acid solution, called *silico-hydrofluoric acid* may be viewed as the *subsesqui-silico-fluoride of hydrogen*, a compound of 157·16 parts or 2 eq. of fluoride of silicon and 59·04 or 3 eq. of fluoride of hydrogen (hydrofluoric acid), as indicated by the formula $3HF + 2SiF_3$. When the solution is neutralized with potassa, the alkali interchanges elements with the fluoride of hydrogen, water and fluoride of potassium are generated, and the latter combines with the fluoride of silicon. This double fluoride consists, therefore, of 157·16 parts or 2 eq. of fluoride of silicon, and 173·49 or 3 eq. of fluoride of potassium, the formula of which is $3KF + 2SiF_3$. A similar change ensues with the protoxides of most other metals, and hence the general formula of the silico-fluorides is $3MF + 2SiF_3$. On exposing these compounds to a red heat fluoride of silicon is disengaged.

Silico-fluoride of Potassium.—This salt falls as a semi-transparent jelly, which has the property of reflecting the colours of the rainbow; but when collected on a filter and dried, it becomes a dense white powder. By evaporating a saturated aqueous solution, it separates in minute anhydrous crystals. It is sparingly soluble in hot water, and still less so in cold water.

The *silico-fluoride of sodium* resembles the former salt, but is much more soluble in hot water. By evaporation it is obtained in minute anhydrous hexagonal prisms. The silico-fluoride of lithium forms similar crystals, but is more soluble in water.

The *silico-fluoride of barium* gradually falls in microscopic crystals, which through a glass appear as elongated prisms, when chloride of barium is mixed with the silico-fluoride of hydrogen, hydrochloric acid remaining in solution. This salt is very sparingly soluble in water whether hot or cold.

The silico-fluorides of strontium, calcium, magnesium, and lead are best prepared by dissolving their respective carbonates in silico-fluoride of hydrogen. The salt of strontium crystallizes in short quadrilateral prisms, which lose their water of crystallization at a gentle heat and become opaque. For complete solubility in water, they require a slight excess of hydrofluoric acid to be present, and then they dissolve freely. The salt of calcium crystallizes in regular quadrilateral prisms. It dissolves readily in water acidulated with hydrofluoric or hydrochloric acids, but is decomposed by pure water, yielding an acid soluble salt, and an insoluble sub-salt. The salts of magnesium and lead are very soluble, and leave a gummy mass by evaporation.

The silico-fluorides of manganese, iron, zinc, cobalt, nickel, and copper are soluble in water, and crystallize in similar hexagonal prisms, probably isomorphous, which contain respectively 1 eq. of the silico-fluoride and 7 eq. of water of crystallization.

TITANO-FLUORIDES.

Hydrofluoric acid dissolves titanic acid, and forms with it an acid solution which may be viewed as the titano-fluoride of hydrogen, consisting of 61·66 parts or 1 eq. of bifluoride of titanium, and 19·68 or 1 eq. of fluoride of hydrogen, expressed by the formula $HF + TiF_2$. When mixed with potassa, water and fluoride of potassium are generated, and the titano-fluoride of potassium results, the formula of which is $KF + TiF_2$. By substituting most other protoxides for potassa similar salts may be prepared, the general formula being $MF + TiF_2$.

Few of the titano-fluorides have as yet been studied. That of potassium crystallizes by evaporation in scales like boracic acid, which are anhydrous, and but sparingly soluble in cold water. The titano-fluoride of sodium is very soluble, and crystallizes with difficulty.

Similar double fluorides may be formed, in which the fluorides of molybdenum, tellurium, and platinum act as the electro-negative ingredients. Few of them, however, have as yet been studied. Berzelius has prepared the alumino-fluorides of potassium and sodium, and the zircono-fluoride of potassium. He employed the latter in the preparation of metallic zirconium. The alumino-fluoride of sodium is found in nature as a rare mineral called *cryolite.*

OXY-FLUORIDES.

Several fluorides combine with oxides in the same manner as chlorides and iodides. An oxy-fluoride of aluminium is prepared as an insoluble gelatinous hydrate by digesting hydrate of alumina in a solution of the sesquifluoride of aluminium. This oxy-fluoride, combined with silicate of alumina, constitutes the topaz. The neutral fluorides of cobalt, nickel, and copper are decomposed by hot water, being resolved into soluble hydro-fluorides, and insoluble oxy-fluorides. Several other fluorides doubtless undergo a similar change. The oxy-fluoride of lead is generated either by digesting fluoride of lead in solution of ammonia, or by fusing together the fluoride and oxide of lead. It is more soluble than the fluoride, and the solution by exposure to the air gives a precipitate of carbonate of oxide of lead. The fluoride of lead also combines by fusion with chloride of lead. Fluoride of calcium forms a very fusible compound with sulphate of lime.

PART III.

CHEMISTRY OF THE COMPOUND RADICALS; OR ORGANIC CHEMISTRY.

By the term "compound radical" is denoted a certain class of compound bodies possessing the property of uniting with the elements, and of forming with them combinations, which are analogous in their properties to the combinations of two simple bodies; combinations therefore in which the elementary body may be removed, and its place occupied by the equivalent quantities of other simple bodies.

The compound radicals are capable of uniting with each other; they form, with oxygen and sulphur, acids and bases; many of them unite with hydrogen, producing *hydracids.*

All organic combinations may be arranged in certain groups, of which their radical forms the origin; the individual members of these groups arise from the combinations of the radical with the elements, and by the union of the compounds thus formed with other compound bodies.

If from any of these combinations one or more of their constituent parts be removed, a new compound of another radical, and sometimes also a new radical in the free or uncombined state, is produced; thus the bisulphuret of cyanogen is decomposed by a temperature of 266° into bisulphuret of carbon, sulphur, and mellone; —4 at. bisulphuret of cyanogen $= N_4C_8S_8$ is decomposed into C_2S_4 (2 at. of bisulphuret of carbon), S_4 and N_4C_6 (mellone). Here the bisulphuret of carbon is a new compound of a simple radical, carbon; and mellone is a new compound radical, analogous to cyanogen in containing the same elements, and forming with the elementary bodies a series of compounds analogous to those of cyanogen. Alcohol from which two atoms of hydrogen have been withdrawn gives rise to aldehyde; $(C_4H_5O + aq.) - 2H = C_4H_3O + aq.$ Here alcohol, the hydrated oxide of the radical C_4H_5 (ethule), by losing 2 at. hydrogen yields aldehyde, the hydrated oxide of a new radical C_4H_3 (acetule).

When the oxygen of any organic compound has been removed, and its place occupied by its equivalent of sulphur, a sulphur-compound of the same radical is formed, and its properties are similar to those of the oxygen-compound. For example, Alcohol $C_4H_5O + HO$ gives mercaptan $C_4H_5S + HS$. Here the formulæ sufficiently show the analogy in composition; and the properties and chemical relations of mercaptan are very similar to those of alcohol, as will be hereafter shown.

Cyanic acid $CyO + HO$, when its oxygen has been replaced by sulphur, gives hydrosulphocyanic acid $CyS + HS$. Here, again, besides the analogy of the formulæ, we find a close correspondence in properties. Both compounds are acids, and their salts have the same relation to each other as that which is found between inorganic oxygen and sulphur salts of the same acid radical; in the case, for example of the salts of carbonic acid CO_2, and those of carbosulphuric acid (bisulphuret of carbon) CS_2.

When the hydrogen of an organic compound is displaced, and its position occupied by its equivalent of chlorine or oxygen, there will be formed either a similar compound of a similarly constituted radical, or several new compounds of a more simple radical.

Aldehyde acted on by chlorine forms hydrochloric acid and chloral.

$C_4H_3O + aq.$ with $Cl_6 = 1$ at. of chloral $C_4Cl_3O + aq.$ and $3HCl$. Here chloral is obviously the oxide of a new radical C_4Cl_3, the constitution of which is similar to that of the radical C_4H_3, of which aldehyde is the oxide; and both the oxide and chloride are further similar in being combined with an atom of water, forming hydrates.

Anhydrous sugar $C_{12}H_9O_9$, in which the 9 at. hydrogen are replaced by 9 at. oxygen, is converted (by being treated with permanganate of potassa) into 6 at. of oxalic acid; for, if the hydrogen be replaced by its equivalent of oxygen, we obtain $C_{12}O_9O_9 = C_{12}O_{18} = 6C_2O_3$. C_2O_3 is the formula of oxalic acid, which is the oxide of a more simple radical.

In like manner, alcohol $C_4H_5O + aq.$ in which the 5 at. of hydrogen are replaced by 5 atoms of oxygen, gives rise to 2 atoms of oxalic acid.

All combinations of compound radicals which do not contain nitrogen, are reduced when exposed to the action of oxygen to oxides of more simple radicals, the higher or lower degree of oxidation being dependent upon the quantity of oxygen present. Thus, by treating alcohol with oxidizing agents, acetal, aldehyde, acetic and formic acids, oxalic acid, carbonic acid, and water may be formed; as the following statement will show.

Alcohol $C_4H_5O + aq.$ is the hydrated oxide of the radical ethule C_4H_5; acetal contains aldehyde; aldehyde $C_4H_3O + aq.$ is the hydrated oxide of the radical C_4H_3; acetic acid $C_4H_3O_3 + aq.$ is a higher degree of oxidation of the same radical; formic acid $C_2HO_3 + aq.$ is the corresponding degree of oxidation of another radical C_2H; oxalic acid C_2O_3 is the oxide of another radical C_2O_2; or it may be viewed as simply a sesquioxide of carbon; carbonic acid CO_2 is a higher degree of oxidation of carbon; and water is the oxide of hydrogen. The two last are, under every circumstance, the products which terminate the action of an excess of oxygen on organic substances.

Organic compounds not containing nitrogen may be decomposed in three different ways when brought into contact with concentrated or anhydrous sulphuric acid; firstly, the acid may withdraw water from the compound, or at least oxygen and hydrogen in the proportion in which they form water; in this case, the other component parts unite into one or more new compounds; thus oxalic acid, acted on by sulphuric acid, gives rise to the formation of water, of carbonic oxide, and of carbonic acid; $C_2O_3 + aq. = CO + CO_2 + aq.$; or secondly, the acid may at the same time give oxygen to a part of the carbon of the compound, when products analogous to the above, together with sulphurous acid, will be produced; or thirdly, the acid may give oxygen to the hydrogen of the compound, and in this case be converted into hyposulphuric acid, which usually enters into very intimate combination with the organic substance thus modified. Instances of both the latter cases will be frequently mentioned hereafter.

Hydrates of organic oxides of basic qualities, when decomposed by an ox-acid, unite with the latter, the water of the hydrate being at the same time liberated. Thus when oxalic acid $C_2O_3 + aq.$ acts on alcohol $C_4H_5O + aq.$ (hydrate of oxide of ethule), water is set free, and oxalic ether $C_2O_3 + C_4H_5O$ is formed. By the action of an hydracid upon the same bodies, a similar decomposition occurs, but it implies the reduction of the oxide; a compound of the radical of the oxide with the radical of the hydracid is produced, while the oxygen of the former unites with the hydrogen of the latter, forming water. Thus alcohol $C_4H_5O + aq.$, when acted on by hydrochloric acid HCl, yields chloride of ethule C_4H_5Cl, and water HO, the water of the alcohol being at the same time set free.

When the action of nitric acid upon an organic compound is of such a nature that only a part of the hydrogen of the latter is removed or is oxidized, it sometimes happens that a new compound, which contains all the carbon of the organic substance, is formed with one of the lower oxides of nitrogen. Some such instances will be hereafter mentioned.

By the action of strong acids upon substances containing nitrogen, there is frequently produced through the medium of the constituents of water, on the one hand ammonia, which combines with the acid, and on the other an oxide of a new radical, in which all the carbon of the original compound is present. For example, hydrocyanic acid H,C_2N, with 1 at. hydrochloric acid HCl, and 3 at. water $3HO$, forms 1 at. hydrochlorate of ammonia (sal-ammoniac) NH_3,HCl, and 1 at. formic acid C_2HO_3. Again, oxamide $C_2O_2NH_2$, with 1 at. sulphuric acid SO_3, and 2 at. water $2HO$, produces 1 at. sulphate of ammonia NH_3,HO,SO_3, and 1 at. oxalic acid C_2O_3. This kind of reaction is very frequent, and of great importance.

All organic compounds not containing nitrogen are decomposed by being fused with hydrate of potash, and if the latter be present in sufficient quantity, the decomposition is not attended with the separation of carbon; the products which are formed are the same as those resulting from the action of powerfully oxidizing agents; water is generally decomposed, its oxygen unites with the carbon and hydrogen of the substance, while its hydrogen is liberated, and either escapes in the form of gas or enters into some new combination. The resulting products of this decomposition may be either ulmic, acetic and oxalic acids, oxalic acid alone, or solely carbonic acid, according to the degree of temperature to which the mixture is exposed. Tartaric acid $C_8H_4O_{10}$ when fused with hydrate of potash is decomposed into water HO, oxalic acid C_2O_3, and acetic acid $C_4H_3O_3$. Paper and wood dust give in the same way oxalic acid and free hydrogen.

All organic compounds containing nitrogen are decomposed by being boiled in a solution of caustic potash, or by being fused with the hydrate; the products are generally the same as those generated by the action of a strong acid upon the same substances, only that with potash the ammonia is liberated, while the oxide of the new carbonized radical enters into combination with the potash. Thus oxamide when acted on by potash, with the aid of water, as above mentioned, yields ammonia and oxalic acid; but in this case the oxalic acid unites with the potash, while the ammonia escapes; whereas, in the reaction with sulphuric acid, the ammonia combines with that acid, while the oxalic acid is liberated, and is deposited in crystals. Many substances which are very rich in nitrogen are converted, with the separation of a part of the nitrogen as ammonia, and the absorption of oxygen, into cyanic acid, and this by uniting with the potash escapes further decomposition; in this case the fused residue is completely decomposed into ammonia and carbonic acid by being dissolved in a little water and boiled; a reaction characteristic of the cyanate of potash.

When organic bodies are exposed to the destructive distillation, their constituents give rise to the production of new volatile compounds of more simple radicals, either with or without the deposition of carbon. The products vary with the temperature, which gives rise to the division of the distillation into several periods. In the first are produced organic acids of more simple radicals, carbonic acid, water, and combustible fluids, which admit of being mixed with water. In the second period, the products of the decomposition of the new substances formed during the first are generated; the acids disappear, their oxygen unites with a part of their hydrogen and carbon, forming more simple compounds, as carbonic oxide, carbonic acid, and water, a portion of the carbon is generally deposited, while the rest unites with hydrogen, giving rise to volatile or fixed oleaginous substances. In the last period, only charcoal and gases are obtained; the latter generally consisting of a mixture of carbonic oxide, olefiant and light carburetted hydrogen gases.

Substances containing nitrogen form, under the same circumstances, ammonia, and sometimes cyanic acid; in the last period, cyanogen and hydrocyanic acid.

When an organic compound is exposed to a similar decomposition in contact with a strong base, which is not reduced to the metallic state, or deprived of carbonic acid by a red heat, it is generally decomposed into carbonic acid, which remains in combination with the base, and into one or more new substances. Should these latter contain oxygen, they may be entirely deprived of it by a new distillation with the base, the oxygen giving rise to another portion of carbonic acid, while the other constituents of the substance are obtained in the form of solid, fluid, or gaseous compounds of carbon and hydrogen.

THEORY OF THE ORGANIC ACIDS.

The relations exhibited in the combinations of the compound radicals have led to new and modified views of the theoretical constitution of chemical compounds in general. It has already been mentioned, that when any substance A, unites with another B, in several proportions, the quantity of B in the second compound is double, and in the third triple, of that in the first. This observation has been raised to the rank of an independent law, but upon a little closer consideration it will readily be seen that it is a necessary consequence of the law of equivalents. Thus, for example, if lead by combining with oxygen forms an oxide which has an affinity to an additional quantity of oxygen, it is impossible that the quantity of oxygen which enters into combination with the first oxide should be a fractional part of an equivalent; but it may be 1, 2, or more equivalents; or 2 equivalents of the protoxide may unite with one of oxygen, and thus a sesquioxide is obtained.

From this manner of viewing the subject, it follows as a necessary consequence, that the second atom of oxygen in the superoxide of lead must be in a state of combination different from that of the oxygen in the oxide; that the sulphuric acid and the peroxide of hydrogen may be considered with great probability of truth as compounds of sulphurous acid with oxygen, and of water with oxygen. Another deduction from this supposition is, that the second equivalent of oxygen in the peroxide of hydrogen, and the third in the sulphuric acid, may be removed, and their place occupied by equivalents of other simple as well as compound bodies. If the third atom of oxygen in sulphuric acid be replaced by an atom of sulphur, the formula for the hyposulphurous acid is obtained; if replaced by an atom of binoxide of nitrogen, the formula for Pelouze's nitro-sulphuric acid is obtained; if by chlorine, the compound discovered by Regnault.

SO_2+O =Sulphuric acid.
SO_2+S =Hyposulphurous acid.
SO_2+Cl =Chloro-sulphuric acid.
SO_2+NO_2=Nitro-sulphuric acid.

If the second atom of oxygen in the peroxide of hydrogen be replaced by an atom of chlorine, the hydrate of chlorine is obtained. If the second atom of oxygen in the peroxide of lead be replaced by an equivalent of chlorine, we obtain the oxychloride of lead $Pb\left.\begin{matrix}O\\Cl\end{matrix}\right\}$. The peroxides of sodium NaO_2 and of calcium CaO_2, yield, by a similar replacement, the bleaching compounds of soda and lime, $Na\left.\begin{matrix}O\\Cl\end{matrix}\right\}$ and $Ca\left.\begin{matrix}O\\Cl\end{matrix}\right\}$. Such compounds have lately been found to be of very frequent occurrence. (Millon.) This view, therefore, not only presupposes the possibility of combinations between simple and compound bodies, but even renders their existence probable.

It will readily be observed, that the capacity of saturation of the sulphurous acid is not changed by its taking up an additional quantity of oxygen, or when this oxygen is replaced by the equivalent of sulphur or binoxide of nitrogen; on this property, therefore, these substances can have exercised no influence.

An attempt has recently been made to apply these views in explaining a certain class of phenomena which frequently present themselves when several of the mineral acids are brought into contact with certain organic combinations, and which consists in this,—that an organic compound is taken up and enters into the constitution of the anhydrous mineral acid without destroying its acid properties, or without changing its capacity of saturation. Examples of this may be seen in anhydrous sulphuric acid and naphthaline, and between the same acid and benzine. In these cases, this explanation may be employed with some degree of probability. But a large number of other compounds is known to which it cannot be applied. In the acid known as the formo-benzoic, we see a compound of formic acid with the oil of bitter-almonds $C_2HO_3 + (C_{14}H_6O_2)$, in which the capacity of saturation of the formic acid has remained unchanged. It is evident that in this substance the oil of bitter-almonds forms a constituent part of the anhydrous acid, but it has not replaced any one of the elements of the latter, as must be presupposed before the above explanation can be applied to the case.

The theoretical opinions of the nature of chloric and iodic acids first proposed by the immortal discoverer of potassium appear to afford a simple and satisfactory explanation of this and other anomalous phenomena. If these views of Davy be applied generally to all hydrated acids, certain general laws may be deduced.

I have already, in the section on salts, given a sketch of these views in a somewhat different form. The student is referred to that section, and in reading the present must bear in mind two general facts there stated: first, that all oxygen acids, in their separate or hydrated state, contain hydrogen, which is generally viewed as forming a part of the hydratic or basic water supposed to be combined with the anhydrous acid; and, secondly, that when a salt is formed by the action, either of what is commonly called a hydrated oxygen acid or of a hydracid, on a metallic oxide, water is uniformly separated. The formation of this water is ascribed to two different sources, by the usual theory, according as the acid employed is an oxygen acid or a hydracid. In that about to be explained, the source of this water is uniformly the same, namely, the combination of the hydrogen of the acid with the oxygen of the oxide.

I. The hydrated acids are certain compounds of one or more elements with hydrogen, in which the latter may be replaced by the equivalents of the metals.

The capacity of such an acid to neutralize a base is consequently dependent upon the quantity of hydrogen which is capable of replacement; but upon this, the other elements of the acid, which together constitute what may be called its radical, can exercise no influence whatever. The capacity of saturation is therefore independent of the constitution of the radical.

II. When therefore the quantity of hydrogen in combination with the radical is increased or diminished, the capacity of saturation will suffer a proportional increase or diminution.

III. Should any quantities, either of the same, or of other elements, enter into the constitution of the radical, while the quantity of hydrogen which admits of replacement be unaltered, the weight of an atom of the acid will be increased, but its capacity of saturation will remain the same; as in the case above quoted of the formobenzoic acid. Formic acid, on this theory, is $C_2HO_4 + H$. An atom of oil of bitter-almonds $C_{14}H_6O_2$ is added to the radical, but does not affect the hydrogen which is capable of replacement, and the capacity of saturation therefore remains unchanged. The formula of the new acid is $C_{16}H_7O_6 + H$.

Salts are, according to this theory, either combinations of the metals with elements, as for example, the haloid salts, or with compound bodies which occupy the place of the element. They may be produced, either by bringing the element in contact with the metal (chlorine and iron), or the hydracid with the metallic oxide (hydrochloric acid with protoxide of iron, sulphuric acid $SO_4 + H$ with protoxide of iron FeO), or an oxacid (SO_3) with a metallic oxide (BaO).

In many instances, where an hydracid neutralizes a metallic oxide, no reduction occurs, or, at least, the newly-formed water is retained in the compound; this water is in a state of combination different from that which may have united with the salt during the act of crystallizing. Such salts, when exposed to the temperature of 212°, lose their water of crystallization; but that which is produced from the oxygen of the oxide and the hydrogen of the acid is retained.

The separation of this water, and consequently the reduction of the oxide and hydracid, may nevertheless be instantly effected by bringing the salt in contact with others which are capable of forming with it a double salt. Hydrochlorate of magnesia MgO,HCl forms with sal-ammoniac (NH_4Cl), the double salt $MgCl + NH_4Cl$. Sulphate of magnesia $MgO + SO_4H$ forms with sal-ammoniac the double salt $MgSO_4 + NH_4Cl$.

The power of a base to neutralize an acid is, according to this theory, dependent not solely upon the position which it occupies in the electrical series, for of two oxides of equal basic properties that which admits of being reduced with the greater ease will possess the greater neutralizing power. The oxide of silver ought consequently to possess this property to a greater extent than any other base; and it is a remarkable fact that in the case of tribasic acids, such as phosphoric and meconic acids where there are 3 atoms of hydrogen capable of replacement, all the three may be replaced by silver with so much facility that the monobasic and bibasic phosphates of silver do not exist; while the tribasic phosphates of potash and soda are formed with difficulty, and the tribasic meconates of these bases are unknown except in solution. Numerous examples of this great neutralizing power of silver have been pointed out by Liebig, and they are inexplicable on the usual theory of that property in bases.

This manner of viewing the subject removes the line of distinction which has been drawn between the haloid and the oxy-salts; it is incompatible with no known fact; in organic chemistry it is of the highest importance to become acquainted with the forms in which it represents the acids and their combinations, inasmuch as it affords us a satisfactory explanation of many phenomena on which the common views can throw no light whatever.

By the term "hydrate of an acid," is meant, therefore, for the future, according to the theory now explained, combinations of one, two, three, or more equivalents of hydrogen, with certain other elements, which, being considered as combined with each other, constitute the radical of the acid. Hydrate of acetic acid is accordingly a compound of H with $C_4H_3O_4$. In the description of the compounds, however, we shall use the usual methods of representation, and consider them, according to the common view, as hydrates of anhydrous acids.

CLASSIFICATION OF THE ORGANIC ACIDS.

The organic acids may be divided into monobasic, bibasic, and tribasic acids.

The monobasic acids combine in their neutral salts with one equivalent of a base, by uniting with which one equivalent of water is separated from the hydrate of the acid. Some of the salts of the monobasic acids combine with other salts of the same class of acids, forming double salts; or with the hydrates of the acid, forming acid salts.

The acid salts of the monobasic acids are decomposed, by being mixed with a solution of other bases, into two or more neutral salts, which may be separated from each other by crystallization, provided they differ from each other in their degree of solubility, and are not isomorphous. To this class belong oxalic acid, &c.

The basic salts of the same acids contain two or more equivalents of a base, by the combination of which with one atom of the acid the same quantity of water is displaced as by a single equivalent of the base.

In the bibasic acid one atom will always unite with two equivalents of a base, which separate from and occupy in the acid the position of two equivalents of water. These two equivalents of base may be, two equivalents of one and the same metallic oxide, or of two different oxides, or one equivalent of a metallic oxide, and one equivalent of a volatile base (water or oxide of ammonium).

The acid salts of this class contain only one equivalent of the acid, which is the cause of there being no separation when they are neutralized by other soluble bases.

The tribasic acids neutralize three atoms of a base; for each atom of a fixed base, which unites with the acid, one atom of water is separated and its place occupied by an atom of a metallic oxide.

The following are the general formulæ for the salts of a monobasic acid. (R represents the anhydrous acid, MO the metallic oxide.)

$R+HO$, hydrate of acid.

$R+MO$, neutral salt.

$(R+MO)+MO$, basic salt.

$(2R+2MO)+MO$, do.

$(R+MO)+2MO$, do.

$$\left.\begin{matrix} R \\ R \end{matrix}\right\} + \left\{\begin{matrix} MO \\ mO, \end{matrix}\right\} \text{double salt with two bases.}$$

$$\left.\begin{matrix} 3R \\ R \end{matrix}\right\} + \left\{\begin{matrix} MO_3 \\ mO, \end{matrix}\right\} \text{double salt with two bases.}$$

$$\left.\begin{matrix}R\\R\end{matrix}\right\}+\left\{\begin{matrix}HO\\MO,\end{matrix}\right\}\text{acid salt.}$$

$$\left.\begin{matrix}2R\\R\end{matrix}\right\}+\left\{\begin{matrix}2HO\\MO,\end{matrix}\right\}\text{acid salt.}$$

General formulæ for the salts of the bibasic acids.

$$R + 2HO,\ \text{hydrate of acid.}$$

$$R + \left\{\begin{matrix}HO\\MO,\end{matrix}\right\}\text{acid salt.}$$

$$R + 2MO,\ \text{neutral salt.}$$

$$R + \left\{\begin{matrix}MO\\mO,\end{matrix}\right\}\text{neutral salt with two bases.}$$

General formulæ for the salts of the tribasic acids.

$$R + 3HO,\ \text{hydrate of the acid.}$$

$$R + \left\{\begin{matrix}2HO\\MO,\end{matrix}\right\}\text{salt with one atom of a fixed base.}$$

$$R + \left\{\begin{matrix}HO\\2MO,\end{matrix}\right\}\text{salt with two atoms of a fixed base.}$$

$$R + 3MO,\ \text{tribasic salt.}$$

$$R + \left\{\begin{matrix}HO\\MO\\mO,\end{matrix}\right\}\text{salt with two different fixed bases.}$$

$$\left.\begin{matrix}R\\R\end{matrix}\right\}+\left\{\begin{matrix}3MO\\MO_3\end{matrix}\right\}\text{double salt.}$$

The monobasic acids rarely yield, when exposed to the destructive distillation, the so-called pyrogenous acids; but, whenever these do happen to be formed, they always possess the properties of a monobasic acid. The bibasic acids very generally give rise under the same circumstances to two new monobasic acids. Thus gallic acid, which is bibasic, yields pyrogallic and metagallic acids, which are monobasic. The tribasic acids yield either three equivalents of a monobasic acid, or two new monobasic acids, or one monobasic and one bibasic acid. For example, when cyanuric acid, a tribasic acid, is heated, 1 eq. yields 3 eq. of cyanic acid, which is monobasic; and meconic acid, which is also tribasic, yields komenic and pyromeconic acids, the former bibasic, and the latter monobasic.

In the following part of the work the organic compounds will be described in the order in which they may be supposed to be developed from their radicals, whether real or hypothetical; to each compound will be attached those new products which arise from its partial decomposition, so that a number of closed groups will be formed, but the individual members of these groups will frequently admit of being deduced from other radicals, and will consequently belong to two or more of the series. This arrangement is not systematic, but it facilitates the comprehension of the changes and metamorphoses which organic substances undergo more than any other.

The known radicals of acids are,—certain compounds of *carbon* and *oxygen*, *cyanogen*, *mellone*, *benzule*, *cinnamule*, *salicule*, *acetule*, and *formule*.

The radicals forming bases are,—*amide*, *ethule*, *methule*, *cetule*, *amule*, and *glycerule*.

The radicals may be distinguished as original or deduced. The latter arise out of the former, either by decompositions, as mellone from sulphuret of cyanogen, or acetule out of ethule; or by being doubled or tripled, as the radicals of fulminic or cyanuric acid out of cyanogen. It is very probable that both benzule and cinnamule are deduced radicals.

AMIDE.

Formula NH_2. Symb. Ad.

This hypothetical combination is considered to be the radical of ammonia. With 1 at. of hydrogen it forms ammonia $NH_2H = NH_3 = AdH$; and with 2 at. of hydrogen it produces ammonium $NH_2,H_2 = NH_4 = AdH_2$. In this work the symbols NH_3 and AdH for ammonia, and those of NH_4 and AdH_2 for ammonium, will be used indiscriminately, since, as above explained, they are exactly equivalent expressions for these compounds. Ammonia may be called *hyduret of amide* or *hydramide*. In the same way as hydracids possess properties similar to those of oxygen acids, so ammonia or hydramide, a hydro-base, has properties analogous to those of oxygen bases.

In all the compounds of ammonia, in which the acid as well as the base may be replaced by other acids or bases, both acid and base contain hydrogen. Where the acid contains no hydrogen, the compound has not the characters of a salt.

If an acid, in general, be represented by the formula XH, then the general formula of these salts is $XH,AdH = XH_2 + Ad$, or $X\,Ad + H_2$. Since amide contains 2 atoms of hydrogen, every salt of hydramide should contain 4. If less hydrogen be present, the compound belongs to a different class.

When a metallic oxide is heated with a salt of hydramide, the hydrogen of the acid unites with the oxygen of the oxide, forming water, which is disengaged with the ammonia, while a metallic salt is formed. $XH,AdH + MO = XM + HO + AdH$.

If the existence of ammonium be admitted, the salts of ammonia will have the general formula X,AdH_2, and will be compounds of ammonium with simple or compound radicals. This view has already been explained in the section on salts. It makes the compounds of ammonium exactly analogous to those of potassium and other metals.

Ammonia, by combining with the elements of 1 at. water, produces oxide of ammonium, and we shall consider the salts of ammonia as formed of this oxide united to anhydrous acids, although it is, perhaps, more correct to consider them as compounds of ammonium with radicals. But the former view is so generally known, that it would be inconvenient at present to change it.

Ammonia.—AdH. This compound has already been described. It is formed in a variety of circumstances where nitrogen and hydrogen meet in the nascent state, especially when nitrogenized organic matters are exposed to heat.

It has the property of combining with a large number of metallic oxides, as formerly mentioned. It also combines with many chlorides, bromides, iodides, and fluorides.

It combines with many anhydrous salts, acting the same part as water of crystallization.

Ammonium.—AdH_2. This compound has not been isolated. It has however been obtained in combination with mercury, forming the amalgam of ammonium, which has all the characters of a metallic compound. By contact with water it is resolved into mercury, ammonia, and hydrogen.

The amalgam is formed by the action of electricity on sal-ammoniac, the negative pole communicating with it through a globule of mercury; or by the action of an amalgam of potassium or sodium on an ammoniacal salt.

Salts of Ammonia or *Oxide of Ammonium.*—These have been already generally described. They are either volatile or decomposable by heat; and when treated with hydrated alkalies, yield ammonia.

They have a great tendency to form double salts with the salts of other bases, many of which have been described in the inorganic chemistry.

Ammonia forms with carbonic acid a great number of different compounds, which have been studied by Rose. Of these, the neutral salt, AdH_2O,CO_2, only exists in solution, or in combination with the others. The bicarbonate, $AdH_2O,2CO_2 + aq.$ is the most stable. Dry ammonia and dry carbonic acid form a peculiar compound, AdH,CO_2, which may be called the anhydrous carbonate, or, more correctly, carbonate of hydramide.

The salt commonly called sesquicarbonate is a compound of the neutral carbonate of oxide of ammonium with the anhydrous bicarbonate. Salt A. $(AdH_2O,CO_2) + (AdH_2O,2CO_2)$. When heated, this salt yields two others, carbonic acid being given off. The first is Salt B, $3(AdH_2O,CO_2) + AdH_2O,2CO_2)$. The second is Salt C, $(AdH_2O,CO_2) + (AdH,CO_2)$. Another salt is obtained when the melted sesquicarbonate is allowed to cool; it is $(AdH_2O,CO_2) + (AdH_2O,2CO_2) + 3HO$. By the action of heat on the salt B, Rose obtained it in two new forms, with 8 at. and with 1 at. water of crystallization. The last of these, when distilled, yields the bicarbonate with 2 at. water; and this, when heated, gives another new salt, $4AdH_2O + 7CO_2 + 8HO$, by losing 1 at. of carbonic acid. When a solution of sesquicarbonate is evaporated in vacuo near sulphuric acid, crusts are formed, the formula of which is $4AdH_2O,9CO_2,5HO$. There are yet other forms of carbonate of ammonia, but the facts above stated are sufficient to show how great a variety of compounds may result from the combination of two substances, although such cases are rare in inorganic chemistry. But carbonic acid and ammonia both belong by their origin to organic chemistry.

COMBINATIONS OF AMIDE.

Amide combines with metals and with some compound radicals. Of the compounds with metals those with potassium and sodium are known in a separate form. They are formed by the action of these metals on dry ammonia, when hydrogen is disengaged, and when put into water they decompose it, producing potash or soda and ammonia. (Gay-Lussac and Thenard.)

The compounds of amide with radicals, when acted on by acids or alkalies, decompose water, producing an acid and ammonia. Thus oxamide, Ad,C_2O_2, with water, HO, yields oxalic acid, C_2O_3, and ammonia, AdH. This class of compounds will be described under the acids which yield them.

The compound of amide and mercury, amidide or amiduret of mercury, forms, according to Kane, compounds with the chlorides, oxides, and salts of mercury, one of which, white precipitate, has been long known, although its composition had not been previously ascertained. The following table contains some of these compounds:—

$AdHg+HgCl_2$ . .	White precipitate.
$AdHg+\left.\begin{matrix}HgO_2\\HgCl_2\end{matrix}\right\}$ . .	Formed by the action of alkalies on the above.
$2AdHg+2SO_3,3HgO_2$	Amiduret with basic sulphate of mercury.
$2AdHg+2NO_5,3HgO_2$	do. do. nitrate of do.
$AdHg+NO_5,2HgO$	Soluble mercury of Hahnemann.

Chloramide of Mercury.—Syn. White Precipitate. This compound is obtained by adding caustic ammonia to a solution of corrosive sublimate. When acted on by boiling water, or by caustic potash, it yields the second compound above mentioned, which is a compound of chloramide and deutoxide of mercury. When too little ammonia is used, there is formed another white compound, in which the salt of alembroth is combined with true white precipitate; $(HgCl_2,2AdH_2Cl)+(AdHg,HgCl_2)$. According to Kane, protochloride of mercury forms a similar compound, which is black. Compounds of amidide of mercury with basic sulphate and nitrate of mercury are given in the table.

When ammonia is added in excess to hot solutions of the salts of copper and silver, crystallizable compounds are produced, in which the metallic amidide is combined with a salt of ammonia. These have been examined chiefly by Kane.

APPENDIX TO AMIDE.

Sulphamide.—Under this name Regnault has described a compound, the formula of which appears to be Ad,SO_2. When heated with acids it yields ammonia, which combines with the acid, and sulphuric acid, which can now be detected in the solution, but not before. It is obtained by exposing the new acid discovered by Regnault, chlorosulphuric acid $=S\left.\begin{matrix}O_2\\Cl\end{matrix}\right\}$, to dry ammonia, when sal-ammoniac and sulphamide are formed.

Sulphohydramide.—This is the compound formed by the combination of dry ammonia and anhydrous sulphuric acid. It is not sulphate of ammonia, and its formula appears to be SO_3,AdH. To form sulphate of ammonia the elements of 1 at. water are wanting. $SO_3,AdH+HO=SO_3,AdH_2O=SO_4,AdH_2$. (Rose.)

Bisulphohydramide.—This is the compound formed by the action of dry ammonia on anhydrous sulphurous acid. By the presence of water it is converted into a mixture of bisulphate and hyposulphite of oxide of ammonium. Its formula is AdH,S_2O_4, which explains this change, for $2\,(AdH,S_2O_4)+2HO=(AdH_2O,$

$2SO_3) + (AdH_2O,S_2O_2)$. When evaporated with an excess of caustic potash, at a certain point of concentration a sudden change occurs: sulphate of potash is deposited, and hyposulphite remains in solution.

Chloramide of Platinum.—A solution of protochloride of platinum in hydrochloric acid, if mixed with ammonia, yields a crystalline green precipitate, which Magnus and Gros found to be $PtCl + AdH$. When this compound is dissolved in nitric acid it is decomposed, platinum being deposited, and the acid is found united to a new compound, having all the characters of an organic base. Its formula is $PtClN_2H_6O$, and it is formed from 2 atoms of the first compound by the loss of 1 eq. platinum and 1 eq. chlorine, the latter being replaced by 1 eq. oxygen.

This body, which may be called chloramide of platinum, forms crystallizable salts with the acids, in which neither chlorine nor platinum can be detected by the usual reagents. These salts are too little known to enable us to give a satisfactory theory of them. But they may be considered not only as salts of a compound base, but as compounds of salts of ammonia with a compound of amide and protochloride of platinum, in which half the chlorine of the bichloride is replaced by amide. Thus the nitrate, $PtClN_2H_6O + NO_5$ may be $\mathrm{Pt}\begin{matrix}\mathrm{Cl}\\ \mathrm{Ad}\end{matrix}\Big\} + (AdH_2O,NO_5)$; that is, a compound of chloramide of platinum with nitrate of oxide of ammonium. For details, the reader is referred to the Memoir of Gros in Liebig's Annalen.

When a current of sulphurous acid is passed through a solution of bichloride of platinum, a period arrives when the solution becomes colourless, and gives no precipitate with sal-ammoniac. If now it be supersaturated with carbonate of ammonia, and concentrated, alcohol precipitates a white crystallizable salt. According to Boeckmann, it contains $2SO_2,2AdH,PtO + HO$, or

$$\mathrm{Pt}\begin{matrix}\mathrm{O}\\ \mathrm{Ad}\end{matrix}\Big\} 2SO_2,AdH_2O.$$

The latter formula contains 1 at. hydrogen less than the former. Both this compound and those above require a thorough investigation.

CARBONIC OXIDE.

Formula CO or C_2O_2.

In certain series of compounds carbonic oxide may be considered as acting the part of a simple substance: viewed in this light it may be considered as producing, by its combination with oxygen, oxalic acid; with chlorine, phosgene gas; with amide, oxamide; and the croconic and rhodizonic acid may be viewed as a product of the decomposition of its compound with potassium. The compounds of this radical are:—

	Formula.	Carbonic oxide.		Equivalent.
Oxalic Acid	$2CO+O$	2 eq.=28·24+1 eq. oxygen=	8	= 36·24.
Chloro-carbonic acid .	$CO+Cl$	1 eq.=14·12+1 eq. chlor. =	35·42	= 49·54.
Oxamide	$2CO+NH_2$	2 eq.=28·24+1 eq. amide =	16·15	= 44·39.
Oxy-carburet of potassium	$7CO+3K$	7 eq.=98·84+3 eq. potas. =	117·45	=216·29.
Rhodizonic acid . . .	$7CO+3HO$	7 eq.=98·84+3 eq. water =	27	=125·84.
Croconic acid	$5CO+H$	5 eq.=70·60+1 eq. hydro. =	1	= 71·60.
Mellitic acid	$4CO+H$	4 eq.=56·48+1 eq. hydro. =	1	= 56·48.

OXALIC ACID.

Discovered by Scheele in 1776. It occurs as a mineral humboldite combined with oxide of iron; in several plants, particularly of the genera oxalis, rumex, &c.; combined with potassa in roots, such as rheum, bistorta, gentiana, saponaria, rumex; with lime, in several kinds of lichens, parmelia cruposa, variolaria, &c. Oxalate of lime is also an ingredient of several urinary calculi; the acid is a product of the decomposition of uric acid, of all organic compounds not containing nitrogen when oxidized by nitric acid, or acted upon by hydrate of potassa (Gay Lussac), or by permanganic acid (Gregory and Demarçay); it is also formed by the decomposition of cyanogen with water and ammonia.

Prep.—1. By digesting by aid of a gentle heat one part of sugar, or better still of potato starch, in 5 parts of nitric acid of sp. gr. 1·42, diluted with 10 parts of water, as long as gaseous products are evolved; by evaporation the acid is obtained in crystals, which may be purified by a second crystallization after being well dried on paper or porous earthenware. When prepared on a large scale, the process is conducted in cylindrical vessels of earthenware, which are heated by being surrounded with warm water; on a small scale it may be made in a porcelain dish. From 12 parts of potato starch 5 of the acid are obtained. The mother liquor should be treated with an additional quantity of acid, and again warmed, when a second crop of crystals will be obtained; this is repeated until the solution is quite exhausted. On account of the cheapness of nitric acid, this is the only process now adopted in the manufactories. Any nitric acid adhering to the crystals may be removed by gently heating them in a porcelain dish, or by repeated crystallization.

2. By precipitating a solution of the superoxalates of potassa by acetate of lead or sulphuret of barium, carefully washing the precipitate, and decomposing it while yet moist by dilute sulphuric acid. A clear solution is obtained by filtration, which must then be evaporated to crystallization. For the purpose of decomposing the precipitated oxalate of lead or baryta, 5 parts of strong sulphuric acid diluted with 10 of water must be employed for every 7 parts of the binoxalate of potassa. Nine-tenths of the dilute sulphuric acid is to be added in successive portions to the moist lead or barytic precipitate; sulphate of lead or baryta is instantly formed, and the oxalic acid is dissolved by the water. After the mixture has stood some hours, the clear liquid should be poured from the precipitate, which should be repeatedly washed. The solution yields, upon evaporation, crystals of pure oxalic acid; any trace of lead may be removed by sulphuretted hydrogen gas. The residue of sulphate of lead or baryta, which still contains some undecomposed oxalate, must be treated with the remaining tenth of the dilute sulphuric acid, and heated with a little more water; in this manner an additional quantity of impure oxalic acid is obtained, but the sulphuric acid may be separated from the crystals by washing.

The production of oxalic acid from organic matter is a consequence of the oxidation of the elements of the latter by the oxygen of the nitric acid; hence those substances give it in greatest quantity which contain oxygen and hydrogen in the same proportion as water. In the formation of oxalic acid by permanganate of potassa 1 eq. sugar ($C_6H_5O_5$) and 3 eq. permanganate of potassa give rise to the production of 3 eq. of oxalate of potassa 3 (KO,C_2O_3), 6 eq. peroxide of manganese ($6MnO_2$) and 5 eq. water ($5HO$). In the double decomposition of oxalate of potassa by sulphuret of barium, sulphuret of potassium, and oxalate of baryta, and in that by acetate of lead, acetate of potassa and oxalate of lead are formed. The oxalate of baryta or lead is decomposed by sulphuric acid, giving rise to free oxalic acid and sulphates of lead or baryta

Prop.—The crystallized oxalic acid is a compound of the hydrate with water of crystallization; it forms colourless transparent oblique rhombic prisms, with one or two terminal planes; one pair of the lateral edges of the latter is sometimes truncated, giving rise to an irregular hexagonal prism, acuminated by 2 or 4 planes;

their sp. gr. = 1·507. It is without odour, tastes and reacts strongly acid, is poisonous. The antidote is chalk or magnesia. The crystals when heated fall into a powder, and lose 28 per cent. = 2 eq. of water of crystallization; the hydrate of oxalic acid is left. When rapidly heated to the temperature of 350° they fuse and lose their water of crystallization, a part of them decomposing, while another portion sublimes as hydrate in dense white fumes of a strong odour, which cover the surface of the fused acid in the form of a woolly crystalline mass. If heated in a retort to 310°, it is completely decomposed into carbonic oxide, carbonic acid, and formic acid, without leaving any residue.

When heated in strong sulphuric acid, it is entirely decomposed into carbonic acid, carbonic oxide, and water. The anhydrous oxalic acid may be considered as a compound of

$$\begin{array}{rl} \text{1 eq of carbonic oxide} \;\; . & C+\ O \\ \text{with 1 eq. of carbonic acid} \;\; . & C+2O \\ \cline{2-2} & 2C+3O \end{array}$$

which accounts for the production of equal volumes of carbonic oxide and carbonic acid, whenever the pure acid or any of its salts is heated in strong sulphuric acid. This decomposition is not attended with the blackening of the acid, or the evolution of any other gas; it furnishes an important means of recognizing and distinguishing the oxalic acid and its combinations from any other substance. When heated with peroxide of manganese or other superoxides, these are reduced to protoxides, which unite with one portion of the oxalic acid, while another portion of it is converted into carbonic acid by the oxygen liberated.

The volume of carbonic acid formed may be used to determine the quantity of oxygen in these oxides.

The crystals dissolve in 8 parts of water at 60°, in their own weight of boiling water, and in 4 parts of alcohol at 60°.

When pure, the oxalic acid is colourless, has no corrosive action on paper, and is not deliquescent: the precipitate, which is formed by salts of baryta, is perfectly soluble in nitric acid; if it contain lead, it is blackened by sulphuretted hydrogen; it should sublime without leaving a residue.

The oxalic acid and its soluble salts are in analytical chemistry the most important reagent for the detection and separation of lime.

In the neutral salts of oxalic acid, the oxygen of the base is to that of the anhydrous acid in the proportion of 1 : 3. If the oxygen of the metallic oxide be considered as a part of the acid, the compound contains carbonic acid and a metal. Many salts of oxalic acid, whose bases are oxides easily reduced to the metallic state, are decomposed by heat into carbonic acid and metal. Thus, the oxalates of nickel and cobalt, when heated in close vessels, yield carbonic acid and pure nickel or cobalt; oxalate of silver is reduced with a slight explosion. The oxalates of the alkalies under the same circumstances evolve carbonic oxide, and are converted into carbonates. Many metallic oxides when heated with an oxalate are reduced by the carbonic oxide gas evolved. All salts of oxalic acid evolve carbonic oxide and carbonic acid gases, when heated in strong sulphuric acid, without being blackened; there exist both neutral and acid salts; the latter contain double, and sometimes four times as much acid as the former.

Formula, $2CO + O$ or C_2O_3; symb. $\overline{O}$; eq. $= 36 \cdot 24$. Dulong, Berzelius.

Of the hydrate . . 1 at. $\overline{O} + 1$ eq. HO eq. $= 45 \cdot 24$.
Of the crystallized 1 at. $\overline{O} + 3$ eq. HO eq. $= 63 \cdot 24$.

Oxalate of Ammonia.—Prep.—By neutralizing a solution of pure oxalic acid by caustic or carbonate of ammonia, or by decomposing the oxalate of lead by sulphuret of ammonium, and evaporating the solution to crystallization. It may also be prepared by neutralizing the bin- or quadroxalate of potassa with carbonate of ammonia; the first crop of crystals consists of oxalate of ammonia, which may be completely freed from potassa by repeated crystallization; the mother liquor contains the neutral oxalate of potassa.

Prop.—Crystallizes in long colourless and transparent prisms of the right prismatic system; of a strong saline taste; is less soluble than the oxalic acid; effloresces in a warm atmosphere, losing 12·6 per cent. of water of crystallization. Is used for the purpose of separating lime from magnesia, and generally for precipitating lime from its solutions. By heat it is decomposed, giving rise to a very remarkable product, oxamide. When a solution of this salt containing chloride of potassium is evaporated to dryness, and the residue is heated to redness, sal-ammoniac is evolved and a part of the potassium remains in the state of carbonate.

Its formula is $NH_4O, C_2O_3 + aq.$ in crystals.

The binoxalate of ammonia $NH_4O, 2C_2O_3 + 2$ aq. is less soluble than the neutral salt. There is also a quadroxalate of ammonia, composed of 4 eq. of oxalic acid, 1 eq. of oxide of ammonium, and 3 eq. of water. (Graham.)

Oxalate of Potassa.—Prep.—By neutralizing the acid salts of commerce, or the pure oxalic acid, by carbonate of potassa, and evaporating to crystallization. By fusing organic matter, as paper, tartaric acid, &c. with hydrate of potassa.

Prop.—Crystallizes in colourless transparent rhombic prisms; is permanent in the air; heated to 160° becomes opaque, and loses 9·7 per cent. = 1 eq. of water, has a cooling bitter taste, is soluble in 3 parts of water, is insoluble in alcohol. (Graham.)*

The formula of the crystals is $KO,C_2O_3 + aq.$; eq. = 92·39.

Binoxalate of Potassa.—Prep.—By neutralizing one part of crystallized oxalic acid by carbonate of potassa, and afterwards adding to the neutral salt another part of oxalic acid, and crystallizing. It was formerly procured by expressing the juice of the oxalis acetosella, clarifying by white of egg or milk, and evaporating to crystallization.

Prop.—Crystallizes in transparent, colourless, oblique rhombic prisms, tastes and reacts strongly acid, is poisonous, is dissolved by 40 parts of cold, and 6 parts of boiling water; is insoluble in alcohol.

When pure, this salt, if heated, should fuse and decompose without emitting a burnt odour, and the residue should be of a grey not a black colour. The presence of cream of tartar is recognized by the carbonaceous residue, and the peculiar odour which it emits on burning; of sulphate of potassa, by the common tests for sulphuric acid. If of two equal parts by weight of the salt, the one be exposed to a red heat, and the other be dissolved in water, the solution of the latter should be deprived of its acid reaction by the addition of the residue of the former; if this does not happen, it is not the binoxalate, but the following salt, which is the only one at present sold in commerce under that name.

It is used and sold as the essential salt of lemons, for removing iron-moulds and other metallic stains (ink, &c.); the following salt may be employed for the same purpose.

The formula of the crystals is $\left\{\begin{matrix} HO,C_2O_3 \\ KO,C_2O_3 \end{matrix}\right\} + 2\,aq.$; eq. = 155·63.

Quadroxalate of Potassa.—Is sold in commerce as binoxalate. It is procured by dissolving the binoxalate in hydrochloric acid, and crystallizing; it is made on the large scale by neutralizing one part of crystallized oxalic acid, and adding to the solution three parts of the pure acid.

---

* The names placed behind the formula denote the chemists from whose analyses they are taken.

Prop.—It crystallizes in colourless transparent prisms of the doubly oblique prismatic system; is as insoluble in water as the binoxalate; loses at 262° two atoms, or 14 per cent. of water; at higher temperatures oxalic acid volatilizes with decomposition. If pure, its reaction when heated is similar to that of the binoxalate; if three parts of the salt be converted into carbonate by a red heat, and added to a solution of one part, the neutral oxalate of potassa should be obtained.

$$\text{Its crystals are} \left\{\begin{matrix} KO,C_2O_3 \\ 3(HO,C_2O_3) \end{matrix}\right\} + 4aq.;\ eq. = 264{\cdot}11 \left\{\begin{matrix} \text{Berzelius.} \\ \text{Graham.} \end{matrix}\right.$$

Oxalate of Soda.—The most insoluble of the soda salts; is with difficulty obtained in distinct crystals, and is always anhydrous; there is a bin-, but no quadroxalate of soda.

Its symbol is NaO,C_2O_3; eq. $= 67{\cdot}54$.

Oxalate of Lime.—*Prep.*—Occurs in several species of lichen, of which it forms the firm hard skeleton, so that many of them, namely the variolaria communis (porophora pertusa) may be used for preparing oxalic acid, but not very advantageously. The pounded lichens should, according to Braconnot, be mixed with one-third their weight of concentrated sulphuric acid, which is diluted with its own weight of water, and the whole boiled for half an hour, separated from the gyps while boiling hot, and the clear solution evaporated to crystallization. The crystals contain lime, and can only be used for preparing the soluble salts of oxalic acid.

The insolubility of the oxalate of lime in water, ammonia, and acetic acid, and its solubility in the nitric and hydrochloric acids, distinguishes it characteristically from most other precipitates. Advantage is taken of this to detect lime in solutions from which all other precipitable metallic oxides have been separated by other means, the alkaline oxalates being the best reagents for this purpose; thus these oxalates are used to separate lime from magnesia, with the latter of which they form soluble double salts. On the other hand, lime may be used to detect oxalic acid; but it must here be remembered that oxalic acid is imperfectly precipitated by salts of lime from a solution which contains the oxides of chromium, iron, or manganese.

Recently precipitated oxalate of lime is a snow-white flocculent powder, insoluble in acetic acid, readily dissolved by free nitric or hydrochloric acid, and by a red heat is converted without being perceptibly blackened into carbonate of lime, from the weight of which, either the oxalic acid, or the lime may be calculated.

Symb. $CaO,C_2O_3 + 2$ aq.; eq. $= 82{\cdot}74$. (Graham.)

Oxalate of magnesia, of oxide of zinc and protoxide of manganese, are analogous in their composition with the salt of lime.

Oxalate of baryta is $BaO,C_2O_3 +$ aq. (Graham.)

Oxalate of Chromium and Potassa.—Discovered by W. Turner, and by Gregory about the same time. Obtained by dissolving by the aid of heat one part of bichromate of potassa, two of the binoxalate of potassa, and two of oxalic acid, and evaporating to crystallize. The solution is accompanied by the rapid evolution of carbonic acid, which is derived from the mutual decomposition of the oxalic and chromic acids, a part of the former being converted into carbonic acid by depriving the latter of half its oxygen. The crystals of the salt are black by reflected, deep blue by transmitted light; the solution green by reflected, and red by transmitted light. Alkalies throw down only a part of the oxide of chromium, and salts of lime produce a very slight precipitate.*

Its symb. is $Cr_2O_3,3C_2O_3 + 3(KO,C_2O_3) + 6$ aq. (Graham.)

Chloro-carbonic Acid.—Discovered by J. Davy, and called by him phosgene. Prepared by exposing equal measures of dry chlorine and carbonic oxide gases to sunshine, when combination ensues in the course of a few minutes, and they contract to half their volume. Diffused daylight causes their union in some hours; but they do not combine at all when the mixture is wholly excluded from light.

Prop.—A colourless gas, has a strong disagreeable odour, excites a flow of tears, and is soluble in water, by which it is decomposed, giving rise to the formation of carbonic and hydrochloric acids. Many metals, when heated in this gas, combine with its chlorine, and liberate the carbonic oxide; several oxides effect the same change, but with the formation of carbonic acid. With alcohol it suffers a very peculiar decomposition; it combines with ammonia, forming a white crystalline solid, which is volatile, and may be sublimed without change, is deliquescent, and is very soluble in water; its symbol is $2NH_3 + COCl$.

Its symb. is $COCl$; eq. $= 49{\cdot}54$. It may be viewed as carbonic acid, in which one-half of the oxygen has been replaced by chlorine.

---

* For an account of the remarkable optical properties of this salt, the reader is referred to a paper by Sir David Brewster in the Edin. Phil. Trans.

OXAMIDE.

The nature of this substance was first developed by Dumas, but it was first obtained by Bauhof by the action of oxalic acid on alcohol. It is formed by the distillation of oxalates with ammoniacal salts, or of oxalate of ammonia; of the greatest purity by decomposing oxalic ether by an excess of a solution of ammonia.

Prop.—A snow-white crystalline powder, void of taste or smell; almost insoluble in alcohol, ether, and cold water, but taken up in small quantity by boiling water; unchanged by dilute, but by concentrated acids or alkalies readily converted with the aid of heat into oxalic acid and ammonia. By the destructive distillation it is decomposed into water, carbonic oxide, hydrocyanic acid, cyanic acid, and ammonia, the two last of which combine and form urea.

If the composition of oxamide be compared with that of oxalate of ammonia, the explanation of its origin and its decomposition will at once be seen.

Oxalate of ammonia is $NH_3C_2O_3 + 2$ aq., subtract the constituents of oxamide . . $\underline{NH_2C_2O_2}$

There is left . . . . $H \quad O + 2$ aq.

Oxamide is formed therefore by the separation of one equivalent of water from the constituents of anhydrous oxalate of ammonia. The oxalic ether is a compound of anhydrous oxalic acid with ether: this compound is instantly decomposed by a solution of ammonia; the oxalic acid gives one eq. of oxygen to one eq. of hydrogen of the ammonia, forming water, which produces alcohol by uniting with the ether; while, on the one hand, carbonic oxide C_2O_2, and on the other amide NH_2 is liberated, and these by combining give rise to the formation of oxamide. $(C_4H_5O, C_2O_3) + NH_3 = NH_2, C_2O_2 + (C_4H_5O + HO.)$

When oxamide is heated in contact with alkalies, which are capable of uniting with oxalic acid, or with acids which will combine with ammonia, one eq. of water is added to its constituents, and it decomposes into oxalic acid and ammonia. The same thing occurs when oxamide and water are exposed to a temperature exceeding 212° under a high pressure. The manner in which oxamide is decomposed by acids is highly interesting, as it appears to throw some light upon certain changes which many organic substances, namely, starch and wood, undergo, by exposure to the action of dilute or concentrated mineral acids, when a certain quantity of water enters into their constitution, and they are converted into sugar. A very small quantity of oxalic acid, for example, will suffice to convert an unlimited quantity of oxamide into neutral oxalate of ammonia, and the oxalic acid, after effecting the change, remains unaltered in the solution; were the new product (oxalate of ammonia) not decomposed by alkalies into its constituents, this decomposition would be exactly similar to the conversion of starch into sugar, and those chemists who suppose the existence of the catalytic force, would be under the necessity of attributing the decomposition of oxamide to that power.

Its symb. is $NH_2 + C_2O_2$; eq. $= 44{\cdot}39$.

RHODIZONIC ACID.

Discovered by L. Gmelin. When a stream of dry carbonic oxide gas is transmitted over a portion of fused potassium, the gas is absorbed in large quantities; the potassium coats the surface of the glass tube, becomes green, and at last a black porous mass is obtained, which, if exposed to the air when warm, inflames, and if covered with water dissolves with the rapid evolution of a combustible gas; if moistened with water it burns, and forms a red solution which contains rhodizonate of potassa. This compound of potassium and carbonic oxide is obtained in considerable quantity as a secondary product during the preparation of potassium, when it separates from the gases evolved in the form of a grey powder, which may readily be collected. Exposed to a moist air it slowly absorbs water, and is converted, without combustion, into rhodizonate of potassa of a scarlet colour; by being treated with alcohol, in which it is insoluble, the free potassa may be separated.

The researches of Heller prove that this potassa salt contains a peculiar acid, the composition of which, according to the analysis of Thaulow, may be represented by the formula $C_7H_3O_{10}$, or $C_7O_7 + 3$ aq., the potassa being supposed to be replaced by water; consequently of carbon and oxygen in the same proportion as in carbonic oxide united with 3 eq. of water. The potassa salt is represented by the formula $C_7O_7 + 3KO$, the lead salt by $C_7O_7 + 3PbO$. The acid is decomposed when an attempt is made to separate it from the oxide of lead by sulphuretted hydrogen; it is obtained mixed with sulphovinate of potassa, when its salt of potassa is decomposed by a mixture of sulphuric acid and alcohol; all its compounds are of a red colour, or, in the dry state, of a brilliant metallic green.

The changes which are produced on rhodizonate of potassa when its aqueous solution is heated are very remarkable; without the evolution of gases it is decomposed into free potassa, oxalate of potassa, and into the potassa salt of a new acid, which has been called the croconic acid by its discoverer L. Gmelin.

Croconic Acid.— If the yellowish-red solution of rhodizonic acid be heated, it acquires a lemon-yellow tint, and deposits, on evaporation, brilliant acicular crystals of a yellow colour; the alkaline solution yields at last oxalate of potassa.

The croconic acid is prepared by adding hydrofluosilicic acid to a solution of its potassa salt, and evaporating to dryness; the pure acid is removed from the yellow residue by water; it is yellow, readily crystallized, tastes and reacts strongly acid, is soluble in water and alcohol; all its salts are yellow, and, with the exception of the ammoniacal salts, are all of them insoluble in alcohol.

The hypothetical anhydrous acid is C_5O_4; the probable composition of the hydrate C_5O_5H.

Croconate of Potassa.—Crystallizes in long six-sided prisms of an orange-yellow colour, and tastes similar to nitre; is neutral with respect to vegetable colours, loses when gently heated 15 per cent. = 2 eq. of water, and acquires a lemon-yellow colour; if heated, burns like tinder into a mixture of carbonate of potassa and carbon, without emitting any burnt odour, but accompanied by the evolution of carbonic oxide and carbonic acid gases; it is decomposed by chlorine and nitric acid with gentle effervescence into peculiar crystalline salts, which have not yet been studied.

The compound of potassium with carbonic oxide contains no rhodizonic acid; the latter is first produced when the former is added to water. The developement of gases rich in hydrogen proves that the potassium is not present in an oxidized state. If the constitution of the potassium compound be represented by the formula $C_7O_7 + 3K$, the rhodizonate of potassa may be considered as formed by the decomposition of three atoms of water. The decompositions do not appear, however, to be quite so simple, for, according to the experiments of E. Davy, the gas evolved is not pure hydrogen, but a new substance, which is distinguished from all known gases by being spontaneously combustible at common temperatures when mixed with chlorine, with the deposition of carbon. Rhodizonate of potassa contains the elements of 1 eq. of oxalate of potassa KO,C_2O_3, 1 eq. of croconate of potassa C_5O_4,KO, and one of free potassa KO, which sufficiently explains its decomposition.

Croconic acid may be considered as a compound of carbonic oxide and hydrogen $C_5O_5 + H$, and stands in this point of view in very close relation with another remarkable acid, namely, the mellitic, which in all its combinations behaves as a compound of a similar radical with hydrogen.

Mellitic Acid.—Discovered by Klaproth. In combination with alumina constitutes a very rare mineral, the honey-stone. Best prepared, according to Wöhler, by decomposing the mellitate of lead by sulphuretted hydrogen. The solution separated by filtration from the sulphuret of lead yields, on evaporation, a white slightly crystalline powder; it is soluble in alcohol, from which it may be obtained by very slow evaporation in radiated groups of acicular crystals. The aqueous solution tastes and reacts strongly acid. The dry mellitic acid is not changed by boiling in nitric or sulphuric acid; boiled in alcohol, it seems to form an acid mellitate of ether. It forms salts by uniting with the base; its alkaline salts are soluble, and may be obtained in crystals, but with the other metallic oxides it forms either insoluble, or very sparingly soluble, compounds. Their general formula when dried at 212° is $MO + C_4O_4H$. When heated they are decomposed, but the silver salt suffers in the first instance a peculiar change; at the temperature of 356° one equivalent of water is separated, and its composition is then C_4O_4Ag. Since the silver salt dried at 212° can retain no water, it is exceedingly probable that the water is first formed at the above heat by the hydrogen of the acid, and the oxygen of the oxide of silver, when the salt passes into a combination of silver and carbonic oxide C_4O_4, the latter acting the part of chlorine or any other haloid substance. By hydrosulphuric or hydrochloric acid unaltered mellitic acid may be obtained.

The silver salt dried at 356° may also be considered as a compound of oxide of silver AgO, with an acid C_4O_3, which differs from oxalic acid by containing a double quantity of carbon.

Formula, $C_4O_4 + H$; eq. $= 57{\cdot}48$.

Mellitate of Ammonia.—Prepared by digesting honey-stone in carbonate of ammonia, when a solution of the salt is obtained and alumina deposited. It crystallizes in two forms, arising probably from different quantities of water; they both belong to the right rhombic system; the crystals are large, brilliant, and transparent; in the air they become opaque and milk-white. They yield by the destructive distillation hydrocyanate of ammonia, and a dark-green sublimate.

Its formula is $NH_3 + C_4O_4H$.

Mellitate of Lead is formed by adding mellitic acid to acetate of lead, or by mixing the mellitate of ammonia with any salt of lead; a voluminous white precipitate is formed, which, when washed and dried, becomes a heavy crystalline powder.

Mellitate of Alumina.—The native crystals, the honey-stone of mineralogists, is found in a stratum of brown coal in Saxony in transparent yellow octohedrons: they are insoluble in cold, but decomposed by hot water, contain 14·5 per cent. of alumina, 41·4 of mellitic acid, and 44·1 of water (Wöhler); therefore 3 eq. of acid, 1 eq. of alumina, and 18 eq. of water.

CARBON AND HYDROGEN.

CYANOGEN.

Cyanogen unites as a compound radical with oyxgen, hydrogen, and most other non-metallic elements, and also with the metals; many of the latter compounds are similar to the haloid salts, but others, on the contrary, possess a perfectly different character. The discovery of cyanogen and its chemical nature, due to Gay-Lussac, has proved of the highest importance for organic chemistry. Cyanogen is composed of 2 eq. of carbon and 1 eq. of nitrogen; its formula is C_2N; symb. Cy; eq. = 26·39.

CYANOGEN AND OXYGEN.

	Cyanogen.	Oxygen.	Water.	Equiv.	Formulæ.
Cyanic acid	26·39=1 eq.+	8=1 eq.		= 34·39	CyO.
Hydrated cyanic acid .	26·39=1 eq.+	8=1 eq.+	9=1 eq.	= 43·39	$CyO+HO$.
Fulminic acid . . .	52·78=2 eq.+	16=2 eq.		= 68·78	Cy_2O_2.
Hydrated fulminic acid	unknown.				
Cyanuric acid . . .	79·17=3 eq.+	24=3 eq.		=103·17	Cy_3O_3.
Hydrated cyanuric acid	79·17=3 eq.+	24=3 eq.+	27=3 eq.	=130·17	$Cy_3O_3,3HO$.

CYANIC ACID.

Hist.—Discovered by Wöhler. Is formed when cyanogen is transmitted over carbonate of potassa at a red heat, or into an alkaline solution; by exposing compounds of cyanogen at a red heat to the action of the air, of nitre, or of peroxide of manganese; by fusing ammelin, melamin, or ammelide with hydrate of potassa; it is a frequent product of the decomposition of compounds of nitrogen. It is not known in the anhydrous state.

Prep.—As hydrate, by distilling dry cyanuric acid or cyamelide in a retort, when the latter is converted into hydrate of cyanic acid, which must be collected in a receiver well cooled by ice.

Prop.—A clear transparent fluid of a strong penetrating odour, similar to that of acetic or formic acid, exceedingly volatile, and causes blisters on the skin, which are accompanied by great pain. Mixes readily with water. Decomposes with the production of great heat shortly after its formation into a white solid of the same composition per cent. (cyamelide); its aqueous solution reddens vegetable colours strongly; it decomposes in the course of a few minutes, together with two equivalents of water, into bicarbonate of ammonia:

$$\left.\begin{array}{ll}\text{Hydrated cyanic acid} = & C_2NO+HO \\ \text{Two eq. water} \;\;. = & 2HO \\ \hline & C_2N \quad H_3O_4\end{array}\right\} = \left\{\begin{array}{ll}\text{2 eq. carbonic acid} = & 2CO_2 \\ \text{1 eq. ammonia} = & NH_3 \\ \hline & C_2NH_3O_4.\end{array}\right.$$

This decomposition with water is the cause of the impossibility of obtaining the free acid from the aqueous solutions of its salts by the action of a stronger acid, although a small quantity, as may readily be recognized by the peculiar odour which accompanies the carbonic acid evolved, does escape decomposition.

The cyanic acid forms only one series of salts with the bases; they are readily recognized by the peculiar decomposition produced by dilute mineral acids. A few moments after mixing the salt with the acid, a rapid effervescence, accompanied by the strong penetrating odour of cyanic acid, is observed, and the solution by being mixed with hydrate of lime evolves ammonia abundantly, which previous to the decomposition cannot be detected. Its salts with the alkaline bases and with ammonia are soluble, the others are insoluble; the former, with the exception of the ammoniacal salt, are decomposed, when their solutions are boiled, into ammonia and carbonates.

Cyanates of Ammonia.—Cyanic acid forms with ammonia two compounds, one of which is particularly remarkable from its identity with urea.

1. *Basic Cyanate of Ammonia.*—When dry ammoniacal gas and the vapour of hydrated cyanic acid are simultaneously conducted into a dry vessel, they unite, forming a white woolly crystalline compound, which contains more ammonia than corresponds to the constitution of a neutral cyanate. It is similar in all its properties to any other salt of cyanic acid; treated with an acid it is de-

composed with effervescence, and alkalies effect the evolution of ammonia; but if on the contrary it be gently warmed, whether dry or in solution, or if it be left for some time exposed to the air, ammonia is given off, it loses all the above-mentioned properties, and is converted into urea.

2. *Anomalous Cyanate of Ammonia; Urea.*—Discovered by Fourcroy and Vauquelin in urine, by Wöhler as the first organic compound artificially produced. It is a constituent of uric acid, and is contained in the urine in combination with lactic acid (Henry). Urea is also a product of the reaction of cyanogen on water when a solution of that gas is allowed to undergo spontaneous decomposition (Pelouze and Richardson).

Prep.—By mixing fresh urine evaporated to the consistence of a syrup at a gentle heat, which should never reach that of ebullition, when still warm, with its own volume of colourless nitric acid of sp. gr. = 1·42. If the evaporation has been carried sufficiently far, the whole will form a thick crystalline mass; to ensure this, a small portion of the urine should be tried from time to time. The crystalline mass consists of a compound of nitric acid and urea, which is sparingly soluble in nitric acid. By the action of the nitric acid on the warm solution heat is developed, and effervescence ensues. This is chiefly owing to the destruction of the colouring matter, and if no external heat is applied, the urea not only is not decomposed, but forms, from the first, nearly white crystals of nitrate. When cold is employed, according to the method formerly recommended, the crystals are very brown, and are purified with difficulty. It is advisable to separate from the inspissated urine as much as possible of the chlorides it contains, by crystallization, before adding the nitric acid (Cap and Henry).

A solution of the colourless crystals of the nitrate of urea is treated with carbonate of baryta until it is rendered perfectly neutral; on evaporating, crystals of nitrate of baryta, and then of urea, will be obtained. The crystals of the latter, by being redissolved in a little cold water, are freed from the last portions of the nitrate of baryta; the solution in alcohol gives crystals of pure urea (Wöhler). Gregory states that coloured crystals of urea are best decolorized by a little permanganate of potash, which destroys the colouring matter, but has no action on urea. Any excess of the salt is removed by alcohol, which converts it into peroxide of manganese.

Instead of using nitric acid, the concentrated urine may be added to a boiling saturated solution of oxalic acid, when the sparingly soluble oxalate of urea falls, which, after being deprived of its colour by charcoal, may be decomposed into the insoluble oxalate of lime and pure urea, by being digested with pounded chalk (Berzelius). It can also be prepared by the decomposition of the cyanate of oxide of silver by sal-ammoniac, or of the cyanate of oxide of lead by pure or carbonate of ammonia.

Prop.—Crystallizes in colourless, transparent, four-sided, somewhat flattened prisms of the sp. gr. 1·35, is soluble in its own weight of cold, and in every proportion in hot water, in 4·5 parts of cold, and in 2 parts of boiling alcohol: the aqueous solution has a cooling bitter taste like nitre; when pure it is perfectly permanent in the air, is not deliquescent, fuses at 250° into a colourless liquid, is decomposed by a higher temperature into ammonia, cyanate of ammonia, and dry solid cyanuric acid. Alkalies do not cause the separation of ammonia in the cold. Unites with several acids without decomposition to crystallizable saline compounds: by evaporating its solution with nitrate of silver or acetate of lead it is decomposed; the products being, with the first, nitrate of ammonia and crystalline cyanate of silver; with the second, acetate of ammonia and carbonate of lead. With hypo-nitrous acid it is instantly decomposed into nitrogen and carbonic acid gases, which are evolved in equal volumes; with chlorine it forms hydrochloric acid, nitrogen, and carbonic acid. When fused with the hydrated alkalies, or heated in concentrated sulphuric acid, it is decomposed together with the constituents of 3 eq. of water into carbonic acid and ammonia. Urea contains the elements of cyanate of ammonia ($NH_4O + C_2NO$); it may also be considered, according to Dumas, as a second compound of carbonic oxide and amide, in which the quantity of the latter is double that in oxamide $C_2O_2 + 2NH_2$.

Nitrate of Urea.—This compound, when recently precipitated from urine, appears in the form of fine crystalline plates of a brown colour and mother-of-pearl lustre; the purer they are, the more they lose this appearance: a solution of pure urea treated with nitric acid gives a granular white crystalline precipitate, which is soluble in 8 parts of cold, but more freely in hot water, from which it crystallizes in broad, scarcely translucent plates; is sparingly soluble in nitric acid, with which it may be boiled without decomposition. Is composed of 1 eq. of nitric acid, 1 of urea, and 1 of water (Regnault).

Cyanate of Potassa.—*Prep.*—By roasting at a red heat dry ferrocyanide of potassium in fine powder upon an iron plate, the powder being constantly stirred; the cyanide of potassium contained in the salt is thus converted, by absorbing the oxygen of the air, into cyanate of potassa. As soon as it is baked into one mass, owing to the fusion of the cyanate of potassa forming, it must be reduced to a fine powder and digested in boiling alcohol, from which, as the solution cools, crystals of the cyanate are deposited. A mixture of two parts of ferrocyanide of potassium, and one of peroxide of manganese, may be treated in the same way. This mixture may be kindled by a red-hot body, when it smoulders away into a brown mass which contains cyanate of potassa, carbonate of potassa, and sesquioxide of manganese. This salt may also be procured of great purity, but not so economically, by fusing the hydrate of potassa in a silver vessel, and adding melam, ammeline, or ammelide in successive portions as long as they are dissolved; the fused transparent mass congeals, on cooling, to a pure crystalline cyanate of potassa.

Prop.—Crystallizes from the alcoholic solution in transparent anhydrous plates, which closely resemble chlorate of potassa, but by exposure to a moist air are gradually converted without any change of form into bicarbonate of potassa, while ammonia is evolved. It is readily dissolved by cold water, in which it spontaneously decomposes into bicarbonate of potassa and ammonia; a change which is accelerated by the application of heat. Fuses at a high temperature without loss of weight to a clear liquid, which, upon cooling, forms an opaque crystalline mass. If a concentrated solution be partially decomposed by acetic acid, or a dilute mineral acid, the acid cyanurate of potassa is precipitated.

Formula $= KO,CyO$; eq. $= 81{\cdot}54$.

Cyanates of oxides of silver and *lead* are white anhydrous salts, which are insoluble in water, and are obtained by precipitating the cyanate of potassa by a neutral salt of lead or silver. Both consist of an eq. of acid and one of metallic oxide; the silver salt is soluble in ammonia, with which it forms a white crystalline compound, but by heat the ammonia is again evolved, and the pure cyanate of silver remains; decomposed by heat when dry, with a slight explosion, into cyanic acid, carbonic acid, nitrogen and dicyanide of silver.

The formulæ are AgO,CyO, and PbO,CyO.

FULMINIC ACID.

Hist.—Shown by Gay-Lussac and Liebig to be the constituent of the fulminating silver and mercury discovered by Howard.

Prep.—This acid is formed when nitrate of silver or protoxide of mercury, with an excess of nitric acid, is boiled in alcohol; aldehyd with nitric ether is evolved, and a white crystalline precipitate, the fulminate of silver or mercury, is deposited from the hot solution. By the action of the nitric acid upon the alcohol, hyponitrous acid on the one hand, and aldehyd and oxalic acid on the other, are produced. The presence of the oxide of silver or mercury effects a reaction between two eq. of hyponitrous acid and one of ether in the alcohol, by which they are converted into water and fulminic acid.

2 eq. Hyponitrous Acid.		Ether.		Fulminic Acid.		Water.
N_2O_6	+	C_4H_5O	=	$N_2C_4O_2$	+	$5HO$.

If a stream of hyponitrous acid vapour be conducted into a solution of nitrate of silver in alcohol, a copious precipitate of fulminate of silver is instantly formed.

Prop.—A bibasic acid; cannot be obtained in a free state from any of its salts, being decomposed at the moment of its separation by any other acid into hydrocyanic acid and a new product. The fulminate of silver is decomposed by hydrochloric acid into chloride of silver, hydrocyanic acid, and a new acid containing chlorine, the hydro-chloro-cyanic acid; similar effects are produced with hydriodic or hydrosulphuric acid. Oxalic and sulphuric acids decompose the salts of silver and copper without effervescence, hydrocyanic acid, ammonia, and other products not yet examined, being formed.

Formula is Cy_2O_2; eq. = 68 78.

Fulminates.—The salts of fulminic acid contain either two atoms of a fixed base (neutral salts), or one atom of a fixed base and one atom of water (acid salts). The two atoms of fixed base must either be two atoms of the same or of two different metallic oxides, which are readily reduced, (2 eq. of CuO, 2 of HgO, 2 of AgO, or 1 eq. of CuO and 1 eq. of AgO, &c.) or 1 eq. of an easily reduced oxide with 1 eq. of an alkali, (1 eq. AgO and 1 eq. KO or BaO, or ZnO, &c.) Fulminates with two atoms of a difficultly reduced metallic oxide cannot be obtained. From this it follows that when a salt of the first class,—such, therefore, as contain 2 eq. of oxides of silver, mercury, or copper,—are brought into contact with an alkali, only one half of the metallic oxide is replaced by its equivalent of the alkali; the other half remains in the new compound. This remarkable property seems to indicate a more intimate connection between the acid and the oxygen of the metallic oxide which is combined with it, than is usually considered to exist. It has already been mentioned, that the salts may be considered as compounds of metals with certain radicals, which arise from the union of the oxygen of the base with the constituents of the anhydrous acid: when, therefore, it so happens that the affinity of the metal for the oxygen with which it is united predominates, it is impossible that the radical should be formed, or, what is the same thing, its decomposition must follow whenever an attempt is made to separate a metallic oxide, which is easily reduced, by one holding its oxygen by a powerful affinity. The composition of the fulminates may be expressed by the following general formulæ:—

a. Neutral Salts . . Cy_2O_2+2MO.
b. Acid Salts . . . $Cy_2O_2+\left.\begin{matrix}MO\\HO\end{matrix}\right\}$.
c. Double Salts . . $Cy_2O_2+\left.\begin{matrix}MO\\mO\end{matrix}\right\}$.

Fulminate of Protoxide of Mercury.—Discovered by Howard.—Prepared by dissolving 1 part of mercury in 12 parts of nitric acid of sp. gr. 1·36, and adding to the solution 11 parts of alcohol of 80—85 per cent.; the mixture must be heated in a water-bath. The fluid soon enters into powerful chemical action; metallic mercury is precipitated, and nitric ether vapours evolved, the latter carrying off along with them a considerable portion of the former; after a short time, hard opaque crystals of fulminate of mercury are deposited. These are carefully washed and dried at common temperatures on paper. It is freed from the admixture of metallic mercury by being redissolved in boiling water, from which it is deposited in white fine acicular crystals of a soft silky appearance. Explodes with great violence when struck or rubbed between two hard substances; placed on a red-hot coal, it burns with a slight explosion and a blue flame. It is used for firing the percussion guns: for this purpose, 10 parts of the salt are reduced to a fine powder by rubbing it with a wooden pestle on a marble slab with 30 parts of water; and this, when mixed with 6 parts of nitre, forms a paste, with which the copper caps are filled.

Formula $=2HgO,Cy_2O_2$; eq. $=488·78$.

Fulminate of Silver.—Prep.—By dissolving 1 part of silver in 10 of nitric acid of sp. gr. 1·36—1·38 at a gentle heat, adding the mixture to 20 parts of alcohol of 85 to 90 per cent., and heating the mixture gently; as soon as the fluid begins to boil, it is removed from the fire, and placed aside to cool. The solution loses its transparency, and deposits the fulminate of silver in fine acicular crystals of a snow-white colour and of great lustre; when washed and dried, their weight should equal that of the silver used.

Prop.—The fulminate of silver is sparingly soluble in cold, but perfectly soluble in 36 parts of boiling water; is not decomposed by nitric acid; more readily exploded than the mercurial salt by friction, a blow, or by contact with concentrated sulphuric acid. Caustic alkalies separate half the silver as oxide; chloride of barium or potassium, as chloride; crystalline salts with two bases are obtained, from which the acid fulminate of silver may be separated by nitric acid; the latter salt may be obtained in crystals, and is more soluble than the neutral fulminate of silver.

Formula $= 2AgO + Cy_2O_2$.

Fulminate of Copper.—Prepared by digesting the fulminates of silver or mercury with metallic copper. It may be obtained in green crystals, which are very soluble, and explode with a green flame.

Formula $= 2CuO,Cy_2O_2$.

Fulminate of Zinc.—According to E. Davy, by digesting the fulminate of mercury with metallic zinc. From the solution, which no longer contains a trace of mercury, baryta precipitates half the zinc, and the fulminate of zinc and baryta $\left\{\begin{matrix} ZnO \\ BaO \end{matrix}\right\} Cy_2O_2$ is obtained; from this the baryta may be precipitated by free sulphuric acid, and the acid fulminate of zinc remains in solution, which has been described by E. Davy as pure fulminic acid, but the presence of the zinc may be shown, after the decomposition of the fulminic acid, by the sulphuret of ammonium and the known reagents (Fehling).

Hydro-chloro-cyanic acid.—Product of the decomposition of fulminate of silver by hydrochloric acid. If hydrochloric acid be added in successive portions to a mixture of fulminate of silver and water the acid fulminate is at first produced; but this salt is afterwards decomposed by the hydrochloric acid into chloride of silver, hydrocyanic acid, and a new acid composed of chlorine, cyanogen, and hydrogen. This substance has a styptic but sweetish taste, does not precipitate silver salts, and is decomposed by heat into carbonate of ammonia and other new products. The same change takes place when it is neutralized by potassa, and the solution evaporated. It contains 5 eq. of chlorine, and its constitution is most probably represented by the formula, $C_2NCl_5 + H_2$.

One eq. of fulminate of silver is decomposed with 7 eq. hydrochloric acid into water, 2 eq. chloride of silver, 1 eq. hydrocyanic acid, and 1 eq. of the new acid.

$$\left.\begin{array}{r} C_4N_2O_2+2AgO \\ \\ +H_7+Cl_7 \end{array}\right\} = \left\{\begin{array}{llll} C_2N & & +H & \text{1 eq. Hydrocyanic acid.} \\ C_2N & Cl_5H_2 & & \text{Hydro-chloro-cyanic.} \\ & & H_4O_4 & \text{4 eq. water.} \\ & Cl_2 & Ag_2 & \text{2 eq. Chloride silver.} \end{array}\right.$$

$$\overline{C_4N_2O_2+2AgO+H_7+Cl_7} = \overline{C_4N_2Cl_7H_7O_4Ag_2}$$

CYANURIC ACID.

Hist.—Described by Scheele as pyro-uric acid, by Serullas as cyanic acid, but its nature was first pointed out by Wöhler and Liebig.

Prep.—It is a product of the decomposition of the solid chloride of cyanogen by water, of the soluble cyanates by dilute acids (acetic, &c.), of urea by heat, of uric acid by the destructive distillation, and of melam, melamine, ammelide, and ammeline by acids. It is best prepared by dissolving dry melam in strong sulphuric acid, by aid of a gentle heat, throwing the solution into 20-30 parts of water; the mixture must be kept for several days at near its boiling heat, until upon trial it no longer gives a white precipitate with ammonia, when the solution may be evaporated to crystallize; the crystals should be purified by a second crystallization. Or it may be made by heating urea beyond its point of fusion, until it is converted with the evolution of ammonia into a white or greyish-white dry mass; this must then be dissolved in concentrated sulphuric acid, the solution treated with nitric acid added drop by drop until it becomes colourless, and then added to an equal volume of water; when cold, crystals of pure cyanuric acid are deposited.

By dissolving melam in strong sulphuric acid it is converted into ammelide, which, by being further heated, is converted into ammonia and cyanuric acid. 1 eq. melam $= C_{12}N_{11}H_9 + 6$ eq. water $= 6HO$, yields 1 eq. ammelide, $C_{12}N_9H_9O_6 + 2$ eq. ammonia, $2NH_3$; and ammelide, in presence of diluted sulphuric acid, is resolved into 2 eq. cyanuric acid, $2(C_6N_3O_3)$ and 3 eq. ammonia, $3NH_3$. Three atoms of urea contain the elements of 1 eq. of cyanuric acid, and 3 eq. of ammonia; at a high temperature the greater part of the ammonia is evolved as a gas, while a small portion remains in combination with the cyanuric acid.

Prop.—Colourless, inodorous, a slight taste, reddens litmus feebly, sparingly soluble in cold, but taken up by 24 parts of boiling water; the crystals from the aqueous solution contain 21·66 per cent. = 4 eq. water, which they lose at common temperature when exposed to the air, but more rapidly when heated, and fall into powder. They are oblique rhombic prisms. The dry acid contains 3 eq. of water; it may be obtained in crystals free from water of crystallization from a hot saturated solution in nitric or hydrochloric acid. The hydrate when heated is converted into 3 eq. of hydrated cyanic acid, the constituents of which it contains. It is soluble in the strongest acids without decomposition, but by long-continued boiling is converted into ammonia and carbonic acid.

It is a tribasic acid; its hydrate is $Cy_3O_3 + 3HO$; eq. = 130·17.

Cyanurates.—The salts of cyanuric acid contain three atoms of base, which are represented in the hydrate by three atoms of water; the oxides of the alkaline metals form salts which contain 1 or 2 eq. of fixed base, with 2 or 1 eq. of water, exactly as in the compounds of phosphoric acid; salts with 3 eq. of a difficultly reduced metallic oxide cannot be procured; the silver salt alone contains 3 eq. of metallic oxide, and is anhydrous; in this state it has the same composition in the 100 parts as the cyanate and fulminate of silver. All cyanurates are decomposed by hydrochloric, nitric acids, &c.; the cyanuric acid crystallizes out of the solutions without retaining a trace of the metallic oxide with which it was united. Its alkaline salts fuse when heated, leaving a cyanate of the alkali, while cyanate of ammonia, cyanic and carbonic acids, are evolved. The general formulæ of the cyanurates are, therefore, as follow:

a. Monobasic Salts . . $Cy_3O_3 + \left.\begin{matrix} MO \\ 2HO \end{matrix}\right\}$.

b. Bibasic Salts . . . $Cy_3O_3 + \left.\begin{matrix} 2MO \\ HO \end{matrix}\right\}$.

c. Tribasic or Neutral Salts $Cy_3O_3 + 3MO$.

Cyanurate of Ammonia.—White, brilliant prisms, which effloresce in the air, and lose ammonia when heated; dried in vacuo, they contain the constituents of 1 eq. of hydrated cyanuric acid, 1 of ammonia, and 1 of water.

Cyanurate of Potassa.—The salt $\left\{\begin{matrix}2HO\\KO\end{matrix}\right\}+Cy_3O_3$ is made by neutralizing a boiling saturated solution of cyanuric acid by potassa; it falls in the form of white brilliant cubes. If these crystals be dissolved in a solution of caustic potassa, the addition of alcohol precipitates the cyanurate of potassa with two equivalents of fixed base, $\left\{\begin{matrix}HO\\2KO\end{matrix}\right\}+Cy_3O_3$, in white acicular crystals. On being redissolved in water and evaporated, it is decomposed into free potassa and the former salt.

Cyanurate of Silver.—If nitrate of silver be added to either of the above salts of potassa, a white precipitate is obtained, which is cyanurate of silver, with 2 eq. oxide of silver and 1 eq. water, $\left.\begin{matrix}HO\\2AgO\end{matrix}\right\}Cy_3O_3$; this salt heated in the dry state evolves hydrated cyanic acid. But if a solution of silver be added to a boiling solution of cyanurate of ammonia, containing ammonia in excess, the cyanurate with 3 eq. of oxide of silver is formed, $3AgO,Cy_3O_3$; it is insoluble in water; very sparingly soluble in dilute nitric acid; may be heated to 600° without decomposition; is white, is not blackened by light, emits carbonic acid and nitrogen gases at a red heat, leaving the cyanide of silver as a residue.

CYAMELIDE, OR INSOLUBLE CYANURIC ACID.

The hydrate of cyanic acid, when free from water of crystallization, hardens shortly after its preparation into a white porcelain-like body, which is insoluble in water, dilute acids, alcohol, and ether; but is dissolved with decomposition by the caustic alkalies; ammonia is evolved, and cyanate and cyanurate of the alkali formed. Concentrated sulphuric acid dissolves it with the aid of heat, when with the elements of 2 eq. water it is decomposed into carbonic acid and ammonia; submitted to the destructive distillation, it is converted into hydrated cyanic acid, a change which is very readily accounted for, since its composition is the same as that of the hydrated acid.

Probable formula is C_2O_2+NH; eq. $=43{\cdot}39$.

CYANOGEN AND HYDROGEN.

HYDROCYANIC ACID, PRUSSIC ACID.

Hist.—Discovered by Scheele; for a knowledge of its nature and chemical properties we are indebted to Gay-Lussac; is a constituent of the water distilled from the leaves and blossoms of several stone-fruits; is formed by the destructive distillation of many substances containing nitrogen, by the decomposition of formate of ammonia by heat, and of the metallic cyanides by acids.

ANHYDROUS HYDROCYANIC ACID.

Prep.—Fifteen parts of crystalline ferrocyanide of potassium are distilled in a retort, at a very gentle heat, with a mixture of 9 parts of sulphuric acid and 9 parts of water, and the products collected in a well-cooled receiver, containing 5 parts of chloride of calcium in coarse fragments: the mixture of acid and water should not be used till perfectly cold. The distillation is stopped as soon as the chloride of calcium is perfectly covered by the fluid collected in the receiver. It is then poured off into a strong glass vessel with a good stopper (Trautwein). It can also be prepared by decomposing the bicyanide of mercury by strong hydrochloric or dry hydrosulphuric acid gas.

The ferrocyanide of potassium contains the cyanide of potassium, which is decomposed by the hydrous sulphuric acid into sulphate of potassa and hydrocyanic acid, according to the equation $KCy + HO,SO_3 = HCy + KO,SO_3$; the latter passes over with a little water into the receiver, but this is absorbed by the chloride of calcium.

Prop.—At common temperatures, a clear limpid fluid, very combustible, burning with a reddish flame, of sp. gr. $= 0{\cdot}6969$ at 64°. It congeals at 5° to a solid fibrous mass, boils at 80°, may be mixed in every proportion with water, ether, and alcohol; the sp. gr. of the vapour is 0·9476: scarcely reddens litmus paper. It has a peculiar penetrating odour, similar to that of bitter almonds, checks the breathing, and causes a flow of tears; it possesses a penetrating taste, which is somewhat burning, and strongly bitter; its vapour, when inhaled, acts instantly as a most powerful poison. The antidotes are ammonia, as likewise chlorine, which, however, must be administered with caution. The congelation of the acid at 5° is, according to Schulz, owing to small quantities of water; he states the perfectly anhydrous acid as still liquid at −64°. Decomposes when perfectly pure with the greatest facility under the influence of light, with the formation of a brown substance and ammonia; small quantities of acids prevent this decomposition; by concentrated mineral acids it is very rapidly converted, together with the elements of water, into formic acid and ammonia; 3 eq. of water and 1 of hydrocyanic acid, a strong acid being present, suffer mutual decomposition and are converted into ammonia which unites with the acid, and into formic acid.

$$\left.\begin{array}{ll}\text{1 eq. hydrocyanic acid} & NC_2H \\ \text{3 eq. water} & H_3O_3\end{array}\right\} = \left\{\begin{array}{ll}\text{1 eq. amm.} & N\,H_3 \\ \text{1 eq. formic acid} & C_2H\,O_3\end{array}\right.$$

$$NC_2H_4O_3 \qquad\qquad NC_2H_4O_3$$

Potassium heated in the vapour of the acid unites with the cyanogen, and liberates the hydrogen; lime and baryta, when heated in the vapour, also liberate hydrogen and give rise to cyanates; it is decomposed by chlorine with the formation of hydrochloric acid and chloride of cyanogen.

HYDROUS HYDROCYANIC ACID.

Prep.—One part of bicyanide of mercury dissolved in 8 parts of water is treated with a stream of sulphuretted hydrogen gas till the latter is in slight excess; the free sulphuretted hydrogen removed by a little carbonate of lead, and filtered. The clear liquid contains $\frac{1}{40}$ of anhydrous hydrocyanic acid. By the decomposition of the bicyanide of mercury the fluid becomes black like ink, and it frequently only becomes clear after the addition of a small quantity of a free mineral acid; it contains too, very generally, small quantities of hydro-sulphocyanic acid. It may be prepared of the same strength and perfectly pure, according to Geiger, by distilling 4 parts of crystallized ferrocyanide of potassium with 18 parts of water and 2 of strong sulphuric acid; 20 parts of water are placed in the receiver, and the distillation is conducted until 38 parts have collected. The distillation is best conducted in a chloride of calcium bath, and the vapours should be condensed by a condensing apparatus of glass. The product is collected in a cylindrical bottle, which is marked at the point corresponding to 38 parts.

According to Clark, it may be prepared by dissolving 1 part of tartaric acid in 40 parts of water, and adding $2\frac{2}{3}$ parts of pure cyanide of potassium in coarse fragments to the solution. The fluid must be kept very cold, and shaken from time to time; this acid contains 3 per cent. anhydrous acid, and $2\frac{1}{2}$ to 3 grs. of bitartrate of potassa in the ounce.

Magendie states that the medicinal hydrocyanic acid is prepared by mixing 1 part by volume of the anhydrous acid with 6 parts of water; or, by weight, 1 part of the acid with $8\frac{1}{2}$ of water. But this would yield an acid containing 12 per cent. of the anhydrous acid, which is four times stronger than the acid usually employed in Britain.

All methods in which hydrocyanic acid is obtained by distillation never yield this energetic preparation of the same quality and strength; even with the application of every possible precaution, the product never contains more than four-fifths of the small quantity of acid which, according to the calculation, ought to be procured; this arises, when ferrocyanide of potassium is used, from a portion of the cyanide entering into combination with the protocyanide of iron during the decomposition of the yellow salt, or from the impossibility of effecting an absolute condensation of so volatile a substance during the distillation. It is therefore greatly preferable to prepare a stronger acid in the first instance, to determine by experiment the quantity of anhydrous acid contained in it; and by the addition of water to bring it to that degree of dilution which is prescribed by the physician, or by the medical laws of the land. For example, 2 parts of crystalline ferrocyanide of potassium are distilled with 1 part of sulphuric acid and 2 of water to dryness in a chloride of calcium bath; and the product, well cooled by the condensing tube apparatus, collected in a narrow-mouthed bottle, into which 2 parts of water have been placed. The quantity obtained generally amounts to 4—$4\frac{1}{2}$ parts by weight of liquid, containing, according to the more or less perfect cooling, from 17—20 per cent. of anhydrous hydrocyanic acid. The exact quantity is determined in the following manner:—One drachm = 60 grs. of the dilute acid is added to a carefully balanced glass vessel, which contains a dilute solution of nitrate of silver, and the increase of weight accurately determined; by way of precaution, a trial is made to see whether the addition of the silver solution causes a further precipitation, the precipitate collected upon a weighed filter, washed, dried, and the quantity of cyanide of silver determined by a second weighing. Five parts of the precipitate correspond to 1 part of the hydrocyanic acid. If, for example, 52 grains of cyanide of silver be obtained, the 60 grains of dilute acid would have consisted of 10·4 grains of anhydrous acid, and of 49·7 grains of water. Were it desired, according to the prescription of any pharmacopœia, to make a hydrocyanic acid containing 3 per cent. of anhydrous acid, and consequently 97 per cent. of water, it is done in the following manner:—3 hydrocyanic acid is to 97 water as 10·4 acid is to X = 336·2 water; to 10·4 grains of anhydrous acid 336·2 grains of water must be added, in order to form a mixture which shall contain 3 per cent. of anhydrous acid. To each drachm of the product, therefore, since it consists of 10·4 grains of anhydrous acid and 49·6 of water, 336·2 — 49·6 = 286·6 grains of water must be added. This method may be used for testing the strength of any solution of hydrocyanic acid; 100 grains of an acid which contains 3 per cent. anhydrous prussic acid should, when precipitated by the nitrate of silver, give 15 grains of the cyanide. This method is independent of all accidents which can possibly have an influence upon the activity of the preparation; it is so very simple that it will yield accurate results in every hand. The peroxide of mercury, which is readily dissolved as cyanide at common temperatures, may also be used to test the strength of the aqueous acid; a drop or two of caustic potassa is added to the solution, which is then treated with a known weight of the peroxide in fine powder; every 4 parts of the oxide dissolved corresponds to one of the anhydrous acid. Testing with green vitriol must be entirely rejected.

Prop.—The properties of the aqueous acid are similar to those of the concentrated, with the difference of taste, odour, and poisonous and combustible properties, which are dependent on a higher or lower degree of concentration; it decomposes when perfectly pure as readily as the anhydrous acid, becoming brown, and at last black. Like the anhydrous acid, however, it may be preserved by adding a trace of a strong mineral acid; a slight permanent reddening of litmus paper should not therefore be considered a sufficient reason for rejecting an acid; it should be clear and colourless, leave no residue on evaporation, nor be precipitated or blackened by sulphuretted hydrogen. Treated with ammonia, and evaporated in a water-bath, the dry residue should not exceed one quarter per cent.; nor should it become brown when heated, this indicating the presence of formic acid, which may also be detected by the tests hereafter to be mentioned. Sulphuric acid is detected by baryta; hydrochloric acid by evaporating in a water-bath till all odour of prussic acid is gone, and then adding a salt of silver. By careful rectification over chalk, an excess of mineral acids may readily be corrected; but in this case a trace of hydrochloric or sulphuric acid must be added afterwards, to give stability to the acid.

Its formula is CyH; eq. = 27·39.

Hydrocyanate of Ammonia, Cyanide of Ammonium.—Prepared by distilling dry ammoniacal salts with metallic cyanides, or by bringing anhydrous hydrocyanic acid into contact with ammoniacal gas, when the compound is produced in the form of bright crystalline plates. It is almost as volatile as the acid itself; decomposes very rapidly in water, is poisonous, and has a strong peculiar smell.

Formula is NH_4Cy; eq. = 44·54.

HYDROCYANIC ACID WITH METALLIC OXIDES.

On bringing hydrocyanic acid into contact with metallic oxides which retain their oxygen by a feeble affinity, as in the oxides of mercury, silver, and palladium, they suffer mutual decomposition, giving rise to the formation of water and a metallic cyanide; if no water be present, the decomposition is accompanied by so great an evolution of heat as to cause an explosion. The alkaline oxides unite with the acid without decomposition, they retain their alkaline re-action, and the solution has the odour of the acid; but also in this class of compounds the decomposition of the acid and alkali is instantly effected, when the solution is treated with another metallic cyanide, with which they form a double compound. With many oxides, as, for example, with the oxide of copper, the hydrocyanic acid gives rise to a corresponding cyanide; but this is decomposed either instantly, or after a short time, into cyanogen gas, and a subcyanide; with the peroxide of lead the protocyanide is formed, and cyanogen liberated.

The compounds of cyanogen with silver, mercury, and most heavy metals, are not decomposed by dilute ox-acids, and are with difficulty decomposed by concentrated nitric acid at a boiling temperature; many of them with great facility by hydrosulphuric and hydrochloric acid into hydrocyanic acid, and a metallic sulphuret or chloride (cyanides of mercury, silver). The cyanides of the precious metals (silver, mercury) are decomposed by heat like the corresponding oxides into cyanogen and metal; the cyanides of the heavy metals into a carburet and free nitrogen; the cyanides of the alkaline metals, if protected from the action of the air and moisture, will bear a very high temperature without decomposition. All insoluble cyanides of the heavy metals may be formed by adding hydrocyanic acid to the acetate. They are decomposed on being heated in a large excess of hydrochloric acid or in hydrate of potassa into a metallic chloride, or into an oxide, ammonia, and formic acid; the latter is the case with the alkaline cyanides when boiled in an excess of alkali. All metallic cyanides, the corresponding oxides of which do not retain carbonic acid at a red heat, evolve, when burnt with oxide of copper, nitrogen and carbonic acid gases in the proportion 1 : 2 by volume.

Cyanide of Potassium.—Formed, when potassium is heated in cyanogen gas with the appearance of combustion, by heating potassium with anhydrous substances containing nitrogen, by heating the carbonate of potassa to redness with matter containing carbon and nitrogen.

Prep.—By adding hydrocyanic acid in excess to a recently prepared concentrated solution of caustic potassa, evaporating the solution in a retort at a boiling heat till crystallization commences, when it must be poured into a porcelain dish and fused at a low red heat. Or a saturated alcoholic solution of hydrate of potassa is treated with the vapour of hydrocyanic acid as long as it throws down a white crystalline precipitate, which should be washed with alcohol and dried. An additional quantity is obtained by evaporating the liquid in a retort; or, better, by heating the ferrocyanide of potassium, carefully dried and reduced to a fine powder, in an iron vessel or well-closed crucible to a strong red heat, exposure to the air being carefully avoided till quite cold; the semi-fused or black porous mass must then be reduced to a fine powder, placed in a funnel, moistened with a little alcohol, and then washed with cold water. The first concentrated colourless solution which passes off, is rapidly brought to dryness and fused in a porcelain dish. The pounded fused mass may also be boiled in spirit when the cyanuret is deposited in crystals on cooling. Alcohol of 60 per cent. dissolves at the boiling temperature a considerable quantity of the cyanide, almost the whole of which is again deposited as the solution cools; if it be stronger or weaker, this does not occur. The application of warm water in the preparation must be altogether avoided, as when air is present it at once colours the solution yellow, owing to the reproduction of the ferrocyanide of potassium.

Prop.—Colourless; crystallizes in transparent cubes, or other forms of the octohedral system, without odour, but of a sharp biting alkaline and bitter-almond taste; fuses readily to a clear transparent liquid, and will bear a white heat without decomposition in close vessels; exposed to oxygen, on the contrary, it is converted into cyanate of potassa. On exposure the crystals become opaque, deliquesce in a moist atmosphere, are very soluble in water, the solution is decomposed even by the carbonic acid of the air, and smells of prussic acid. Even kept in close vessels it decomposes in a shorter or longer time.

The cyanide of potassium is converted, when dissolved in water, into hydrocyanate of potassa; if the solution be evaporated with an excess of potassa, the whole of the nitrogen is evolved as ammonia, and formate of potassa remains. Effervescence on the addition of an acid proves the presence of carbonic acid; a yellow colour, that of iron; and a blackening when heated, the admixture of salts of formic acid. It may be used instead of the hydrocyanic acid.

Formula $= KCy$; eq. $= 65{\cdot}54$.

Cyanide of sodium may be prepared in the same manner, and has the same properties as the cyanuret of potassium.

Formula $= NaCy$.

Cyanide of Zinc.—Prep.—Metallic zinc is dissolved by the aid of heat in acetic acid, and the acid solution treated with hydrocyanic acid as long as a precipitate is formed; the latter must then be washed and dried.

Prop.—A brilliant white, tasteless powder, insoluble in water and alcohol, but perfectly soluble in ammonia, as also in dilute hydrochloric acid with the evolution of hydrocyanic acid.

Formula $= ZnCy$; eq. $= 58{\cdot}69$.

Cyanide of Iron.—This compound, remarkable from its tendency to form a very peculiar class of double compounds by uniting with other cyanides, would appear as incapable of existing in a free state as the corresponding protoxide. On adding a proto-salt of iron to a solution of cyanide of potassium, a yellowish-red precipitate is formed, which is re-dissolved by an excess of the cyanide into a yellow liquid, the ferrocyanide of potassium. On heating dry ferrocyanide of ammonium, cyanide of ammonium is evolved, and a grey insoluble powder, which has been considered as this compound, is the residue obtained. It is also produced, according to Robiquet, by pouring a saturated solution of hydrosulphuric acid over recently precipitated Prussian blue contained in a well-stoppered vessel; the Prussian blue becomes white, and the solution contains hydrocyanic acid. (Berzelius.) The properties of these preparations differ too widely to allow of their being considered as identical.

Formula $=$ FeCy; eq. $= 54{\cdot}39$.

Sesquicyanide of Iron.—Unknown in a pure state. On mixing a solution of ferridcyanide of potassium to the silico-fluoride of iron, the silico-fluoride of potassium is separated, and a deep brown liquid remains, which has a strong astringent taste, becomes blue on evaporation, and leaves a residue of Prussian blue. It forms a numerous class of double cyanides. Its formula is Fe_2Cy_3; eq. $= 135{\cdot}17$.

$\frac{4}{3}$ *Cyanide of Iron.*—This compound is obtained by boiling the green powder, which falls on heating or exposing to the air a solution of ferrocyanuret of potassium charged with an excess of chlorine gas, with $8-10$ times its weight of concentrated hydrochloric acid, until the filtered solution ceases to be rendered turbid by water. The green residue, when well washed, should be dried in vacuo; it is but slightly acted upon by concentrated hydrochloric acid, or by chlorine, but it is readily decomposed by hydrate of potassa into peroxide of iron and ferrocyanide and ferridcyanide of potassium. (Pelouze.)

Its formula is $FeCy + Fe_2Cy_3 + 4$ aq.

Cyanide of Cobalt.—Formed by mixing a solution of the acetate of cobalt with hydrocyanic acid. It is a brownish-white precipitate.

Formula $=$ CoCy; eq. $= 55{\cdot}89$.

Bicyanide of Mercury.—Prep.—An aqueous solution of prussic acid is treated with finely powdered peroxide of mercury until all odour of the former disappears; the liquid yields on evaporation perfectly pure crystals of the bicyanide. For this purpose the acid prepared as recommended by Geiger is most convenient; it should be introduced into a well-stoppered bottle, and the combination with the oxide of mercury promoted by frequent agitation. It must always be remembered, that the compound can only be produced when water is present in sufficient quantity to dissolve the whole of the cyanide; water must therefore be added, should it be observed that the liquid smells of prussic acid, while any portion of the oxide of mercury remains undissolved. Or by adding to a solution of 2 parts of ferrocyanide of potassium in 15 parts of boiling water, 3 parts of perfectly dry bisulphate of the peroxide of mercury; boil the mixture for a quarter of an hour, and separate the clear liquid while boiling hot from the precipitate by filtration; as the solution cools, the bicyanide crystallizes. The mother-liquor yields a second crop of crystals by further concentration; or it may be evaporated to dryness, and the cyanide obtained from the residue by boiling alcohol. The first crystals from the aqueous solution are purified by a second crystallization. The formation of the cyanide in this process is owing to the mutual decomposition between the 2 eq. of cyanide of potassium of the ferrocyanide and 2 eq. of persulphate of mercury into bicyanide of mercury and sulphate of potassa, while the cyanide of iron is precipitated.

Prop.—Crystallizes in colourless transparent regular four or six-sided prisms; they are anhydrous, permanent in the air, of a very disagreeable metallic taste, and are very poisonous. Is dissolved by 8 parts of water at 60°, but is more soluble in boiling water, and in alcohol.

Peroxide of mercury decomposes all soluble metallic cyanides with the formation of an oxide and double cyanides of mercury and other metals. If the bicyanide be boiled with an excess of peroxide of mercury, the latter is dissolved in large quantity (3 eq. Kühn), and the solution on evaporation deposits a compound in fine acicular crystals; these are more soluble in cold water than the bicyanide, and have an alkaline reaction on vegetable colours. The formation of this compound, during the preparation of the bicyanide, must be carefully avoided, or only a white saline mass may be obtained. This is best done by the careful addition of hydrocyanic acid until its odour is slightly perceptible.

A cyanide corresponding to the protoxide of mercury is unknown. When an attempt is made to obtain it by adding a protosalt of mercury to hydrocyanic acid, metallic mercury is instantly separated, and the bicyanide formed.

Formula is $HgCy_2$; eq. $= 254 \cdot 78$.

Cyanide of Silver.—Falls, on mixing a soluble salt of silver with hydrocyanic acid, in the form of a brilliant white curdy precipitate; is decomposed by all hydracids, but with great difficulty by other mineral acids; strong boiling nitric acid alone can dissolve it; suffers no change by the caustic fixed alkalies, is readily dissolved by ammonia. Is soluble in a concentrated solution of the nitrate of silver, forming with it a compound, which may be obtained in crystals, but is not permanent in water. It gives rise to double compounds with all cyanides of the alkaline metals.

Formula is $AgCy$; eq. = 134·39.

Cyanide of Palladium.—The affinity of palladium for cyanogen surpasses that of all other metals; they combine, whenever hydrocyanic acid or any soluble cyanide is added to a salt of the oxide of palladium, in the form of a light chestnut precipitate, which has a greenish tint if copper be present; gives rise to double salts with ammonia, cyanide of potassium, and nitrate of the oxide of palladium.

Formula, $PdCy$; eq. = 79·69.

Percyanide of Gold.—For the preparation of this compound, which has recently been used medicinally, a solution of gold in aqua regia, carefully deprived of all free acid by evaporation, is precipitated by a recently prepared solution of caustic potassa to which hydrocyanic acid has been added in excess; care must be taken that a small quantity of the chloride of gold remain in the solution. The yellowish-white precipitate is collected, washed, and dried. An excess of cyanide of potassium dissolves the precipitate, and the solution has a yellowish-red colour, but in this case it is re-precipitated by the addition of an acid. It may also be prepared by adding to 16 parts of gold dissolved in aqua regia by the aid of heat a boiling solution of 24 parts of bicyanide of mercury, evaporating to dryness, and washing with pure water. The cyanide corresponding to the oxide does not exist.

Its formula is $AuCy_3$; eq. = 278·17.

DOUBLE CYANIDES OF THE METALS.

All insoluble metallic cyanides (of heavy metals) combine with the soluble (of alkaline metals) to peculiar generally crystallizable double compounds, which are very similar in their general properties to the combinations of the soluble and insoluble metallic sulphurets. For example, the cyanides of gold, palladium, silver, nickel, zinc, copper, &c., are readily dissolved by the cyanide of potassium or sodium; the solutions are either yellow or colourless, and are not changed or decomposed by the caustic or carbonated alkalies, or by metallic chlorides; acids cause the precipitation of the insoluble cyanide, owing to the decomposition of the soluble cyanide. On mixing a double cyanide of potassium or sodium with a metallic salt, the basis of which is an oxide of a heavy metal, a new double compound is generally formed, arising from the replacement of the alkaline metal by its equivalent of the heavy metal. The double cyanuret of silver and potassium, $KCy + AgCy$, forms, with acetate of lead, $PbO,\bar{A}$, the double cyanide of silver and lead, $PbCy + AgCy$, and acetate of potassa.

The soluble metallic cyanides also very frequently form double compounds with the insoluble metallic chlorides, bromides, and iodides.

The double compounds of both the cyanides of iron and the cyanide of cobalt with other cyanides, and with hydrocyanic acid, are quite unique in their properties; the latter are soluble in water, are crystallizable, are possessed of a distinct acid taste, produce a permanent reddening of the vegetable colours, decompose carbonates with effervescence, and perfectly neutralize the alkalies; properties not possessed by the free hydrocyanic acid. Neither the iron nor the cobalt in these compounds can be detected by the alkalies, by the soluble metallic sulphurets, or, in short, by any of the ordinary reagents.

Constitution of the double compounds of Iron and Cyanogen.— The composition of these compounds is best explained by supposing the existence of a radical, which contains 1 eq. of iron in combination with carbon and nitrogen in the same proportion as they exist in cyanogen, but in such quantity as would form 3 eq. of the latter, and which radical, by uniting with 2 eq. of hydrogen, forms a bibasic acid. The radical itself may be called ferrocyanogen; the acid, hydro-ferrocyanic acid; and the compounds of the radical with the metals by the same adjuncts to ferrocyanide as are used for the corresponding oxides.

The ferrocyanogen is composed of

$$\left.\begin{matrix}\text{6 eq. carbon}\\ \text{3 eq. nitrogen}\end{matrix}\right\}=\text{3 eq. cyanogen}+\text{1 eq. iron}=\text{1 eq. ferrocyanogen.}$$

Its symbol is Cfy, and its compounds are

Hydro-ferrocyanic acid	$Cfy+H_2$
Ferrocyanide of potassium	$Cfy+K_2$
Ferrocyanides with two basic metals	$Cfy+\left\{\begin{matrix}K\\ Ca\end{matrix}\right\}$ or $\left\{\begin{matrix}K\\ Ba\end{matrix}\right\}\begin{matrix}K\\ St\end{matrix}\left\{\begin{matrix}K\\ Mn\end{matrix}\right.$
Ferrocyanide of potassium and iron	$2Cfy+\left\{\begin{matrix}Fe_3\\ K\end{matrix}\right.$
Prussian blue	$3Cfy+2Fe_2$
Basic Prussian blue	$3Cfy+\left\{\begin{matrix}2Fe_2\\ Fe_2O_3\end{matrix}\right.$
Soluble Prussian blue	$2Cfy+\left\{\begin{matrix}Fe_2\\ K\end{matrix}\right.$
Ferrocyanide of zinc and potassium	$2Cfy+\left\{\begin{matrix}Zn_3\\ K\end{matrix}\right.$

HYDRO-FERROCYANIC ACID.

Discovered by Pornett. Prepared by decomposing recently precipitated ferrocyanide of lead or copper by sulphuretted hydrogen; filter to separate the metallic sulphuret, and evaporate over sulphuric acid in vacuo. (Berzelius.) Or by mixing pure Prussian blue with ten times its volume of concentrated hydrochloric acid, and as soon as the blue colour has disappeared, and the insoluble portions have become yellow or brown, washing it well with fresh portions of the concentrated acid; the moist mass should be spread out upon a clean tile, placed under a bell-jar with quick lime, and when dry dissolved in alcohol, and the solution spontaneously evaporated. (Robiquet.)

Prop.—A white distinctly crystalline mass, or small granular, sometimes acicular crystals, which acquire a blue colour by exposure to the air. The aqueous solution is decomposed by boiling into hydrocyanic acid, and a white, but after exposure in open vessels blue, precipitate. The hypothetical radical of the acid can (probably) not be isolated. Its formula is $Cfy + H_2$; eq. $= 109{\cdot}17$.

Ferrocyanide of Ammonium.—It may be formed by digesting at a gentle heat the ferrocyanide of lead with carbonate of ammonia; filtering to separate the carbonate of lead, and evaporating to crystallization. It is isomorphous with the ferrocyanide of potassium; the crystals are white, or yellowish-white, transparent, permanent in the air, very soluble in cold, but decomposed by boiling water into cyanide of ammonium and cyanide of iron, insoluble in alcohol. It forms with sal-ammoniac a double salt, which is obtained by boiling a solution of equal parts of ferrocyanide of potassium and sal-ammoniac in 6 parts of water, when it forms, on cooling, large lemon-yellow crystals, which are very brittle and permanent in the air. They are composed of an eq. of ferrocyanide of ammonium, 1 of sal-ammoniac, and 3 eq. water. (Bunsen.)

HYDRO-FERROCYANIC ACID AND METALLIC OXIDES.

On bringing the hydro-ferrocyanic acid into contact with metallic oxides, the latter are reduced by the hydrogen of the acid, water, and a compound of the metal with the radical of the acid being formed; as 1 eq. of the acid contains 2 eq. of hydrogen, it follows as a necessary consequence that it decomposes 2 eq. of the most numerous class of oxides, in which 1 eq. of oxygen is present in 1 eq. of the oxide.

The ferrocyanides are, without exception, decomposed when exposed to a red heat in close vessels; those which contain an alkaline metal give rise to the formation of the cyanide of that metal, a carburet of iron, and the evolution of nitrogen gas; all others yield mixtures of metals and metallic carburets, with or without the evolution of cyanogen. All the soluble ferrocyanides are decomposed by being boiled with peroxide of mercury into bicyanide of mercury, free alkali, and oxy-cyanide of iron. The ferrocyanides of potassium and sodium are converted by being calcined in open vessels into alkaline cyanates, and the black oxide or carburet of iron.

Most of the ferrocyanides contain water of crystallization, which they lose when heated. Those of zinc, copper, and mercury unite with ammonia to peculiar crystalline double compounds. (Bunsen.) Most of them are soluble in concentrated sulphuric acid without decomposition; or they unite with it, when they lose their colour, to saline combinations in which the ferrocyanide acts the part of a base. By nitric acid they are decomposed, many of them with the evolution of cyanogen and the formation of metallic ferrid-cyanides. When those which are soluble in water are boiled with dilute acids, the hydro-ferrocyanic acid is separated, and at that temperature decomposed into hydrocyanic acid which escapes, and into the white but impure protocyanide of iron, which, on exposure to the air, absorbs oxygen and becomes blue.

Ferrocyanide of Potassium.—Prep.—This compound occurs of great purity in commerce, and is prepared on a large scale by fusing substances which are rich in nitrogen, as horn, hoof, and dried blood, with 2—3 parts of carbonate of potassa in iron vessels; the mass after perfect fusion is allowed to cool, the soluble parts removed by boiling water, from which the ferrocyanide is obtained by crystallization. It may be obtained on a small scale by boiling Prussian blue in carbonate of potassa.

By the fusion of substances containing carbon and nitrogen with carbonate of potassa at a red heat, the potassa is reduced by a portion of the carbon to potassium, by the reaction of which on the rest of the materials cyanide of potassium as the principal product is formed. The red-hot fused mass does not contain a particle of the ferrocyanide, but it contains, in the form of a black slime, a large quantity of finely divided metallic and carburetted iron. If the mass be treated with cold water, and the solution evaporated, no ferrocyanide is obtained; but if, while covered with water, it is freely exposed to the air and gently warmed for some hours, oxygen is rapidly absorbed, and a yellow solution is obtained, which is rich in ferrocyanide of potassium; this arises from the solution of pure cyanide of potassium dissolving iron when oxygen is present with the formation of potassa; the potassium, therefore, of the cyanide, by uniting with oxygen, gives the cyanogen to the iron, by which the latter is converted into cyanide, and thus acquires the property of uniting with undecomposed cyanide of potassium to form the ferrocyanide. In close vessels the solution of iron by cyanide of potassium is attended with the evolution of hydrogen, owing to the decomposition of water, the oxygen of which unites with the potassium, while the cyanogen passes over to the iron. The fused mass contains a large quantity of free potassa, which, by being boiled with the cyanide of potassium, causes the decomposition of the latter into formiate of potassa and ammonia; if the animal substances be fused in open vessels with the potassa, a portion of the cyanide of potassium is burnt into cyanate of potassa, the solution of which is decomposed by boiling into ammonia and bicarbonate of potassa. The ammonia arises in every case from the decomposition of the cyanide of potassium; its formation is consequently always accompanied by a corresponding loss, and should be most carefully avoided.

It is best to treat one-third either by volume or weight of a cold solution of the raw mass with protosulphate of iron as long as a precipitate falls, then add the remaining two-thirds of the solution, and bring the whole to the boiling point; it must always be remembered that the solution should contain free potassa. In this manner sulphate of potassa is obtained, and all the cyanide of potassium is converted without any loss into the ferrocyanide; the solution can be evaporated without decomposition, and the sulphate of potassa is easily separated by crystallization. The raw solution generally contains some sulphocyanide of potassium, sulphuret of potassium, formiate and carbonate of potassa, all of which remain in the mother-liquor.

Prop. — Crystallizes in large quadrangular tables or short prisms with truncated edges and angles, which belong to the square prismatic system; is of a lemon-yellow colour, of sp. gr. 1·832; has at first a sweetish bitter, but afterwards saline taste;

is permanent in the air, loses at 212° 12·82 per cent. = 3 eq. of water, and becomes white; is soluble in 4 parts of cold and in 2 parts of boiling water; is insoluble in alcohol, by which it is precipitated from its aqueous solution in brilliant yellow flakes. Is converted by nitric acid, with the escape of cyanogen, and by chlorine, into the ferrid-cyanide of potassium. At a red heat it is decomposed into the carburet of iron and cyanide of potassium, but by the action of atmospheric air the latter is converted into cyanate of potassa.

The ferrocyanide of potassium forms double compounds with other ferrocyanides. It is used as a test for the oxide of iron in solution. When thus employed, however, it must be remembered that the solution must not have an alkaline reaction, for all solutions of oxide of iron which contain free ammonia are not precipitated by the ferrocyanide of iron.

It is used for the preparation of hydrocyanic acid, bicyanide of mercury, Prussian blue, &c.; taken in large doses is purgative, and not poisonous.

The crystals are $K_2Cfy + 3$ aq.; eq. = 185·47.

Ferrocyanide of Sodium.—Prepared by boiling Prussian blue with carbonate of soda. Crystallizes in yellow quadrangular prisms, effloresces in the air, contains 59 per cent. = 12 eq. of water of crystallization, is soluble in 4½ parts of cold water, is insoluble in alcohol.

Ferrocyanide of Barium.—Prepared by digesting Prussian blue in a solution of baryta. Is deposited from the boiling hot solution in small rhomboidal crystals of a yellow colour, is soluble in 100 parts of boiling and 1920 parts of cold water; loses at 100° 16·58, at higher temperatures 18 per cent. = 6 eq. of water; is soluble in concentrated sulphuric acid.

Ferrocyanide of Iron.—Unknown in pure state, but exists in the double ferrocyanide; see those of potassium.

Ferrocyanide of Lead.—Prepared by mixing a soluble salt of lead with ferrocyanide of potassium. Falls as a white precipitate with a shade of yellow. When dry it is anhydrous, Pb_2Cfy.

Ferrocyanide of Zinc.—Prepared by mixing a soluble salt of zinc in solution with hydro-ferrocyanic acid. It falls as a white precipitate.

Ferrocyanide of Copper.—Prepared by mixing a soluble salt of copper with ferrocyanide of potassium. A beautiful red brown precipitate, which is insoluble in dilute acids; a solution containing $\frac{1}{60000}$ of its weight of oxide of copper is readily recognized by the distinct reddish-brown colour produced by ferrocyanide of potassium.

Ferrocyanide of Mercury.—On mixing a solution either of proto- or peroxide of mercury with ferrocyanide of potassium a white precipitate falls, which spontaneously decomposes into cyanide of mercury which is re-dissolved, and into cyanide of iron. This change is rendered more rapid by the aid of heat, and metallic mercury is separated when a proto-salt of mercury has been used.

Ferrocyanide of potassium produces white precipitates with the salts of silver, zinc, and bismuth, a greenish-white with those of nickel, and green with cobalt; but the latter, by taking up water, become reddish-grey; with salts of protoxide of manganese a white precipitate is first formed, but it afterwards acquires the colour of peach-blossoms.

Sesqui-ferrocyanide of Iron.—Discovered by Diesbach in Berlin in 1710, from which it became generally known as Prussian or Berlin blue. It is formed whenever a salt of peroxide of iron is added to a soluble metallic ferrocyanide; compounds similar in colour, but different in constitution, although likewise known by the name of Prussian blue, may be obtained by precipitating the ferrid-cyanide of potassium by a salt of the protoxide of iron, or by precipitating the ferrocyanide of potassium by a proto-salt of iron, adding an acid, and exposing the precipitate to the air until it becomes blue.

Prep.—By precipitating a solution of perchloride or pernitrate of iron by ferrocyanide of potassium, care being taken to avoid an excess of the latter; or, by dissolving 6 parts of green vitriol and 6 parts of ferrocyanide of potassium, each by itself, in 15 parts of water, mixing the two solutions, and then adding to them 1 part of concentrated sulphuric acid and 24 parts of fuming hydrochloric acid under constant stirring. After some hours the whole should be treated with a clear solution of 1 part of bleaching powder in 80 of water, added in successive portions, care being taken to stop the addition of the bleaching liquid as soon as an effervescence arising from the escape of chlorine gas is observed. After standing some hours, the precipitate should be thoroughly washed and dried, either at common or high temperatures. Or the precipitate may be treated with dilute nitric acid till it is rendered of a deep blue colour. This yields the finest product. (Hochstätter.)

Prop.—Prussian blue dried at common temperatures is a light porous body of a deep velvet-blue colour; dried, on the contrary, at high temperatures, it has a deep copper-red colour, but the powder is blue; it is tasteless, insoluble in water and dilute acids, and is not poisonous. The painters' Prussian blue of commerce contains variable quantities of earthy matter. When heated in close vessels, water, hydrocyanic acid, and carbonate of ammonia are evolved, and carburet of iron is the residue; it may be kindled in the air by a red-hot body, when it burns slowly to oxide of iron; it is decomposed by fuming nitric acid, but strong sulphuric acid unites with it, forming a white mass of the consistence of paste. Concentrated hydrocyanic acid deprives it of its iron, and liberates the hydro-ferrocyanic acid; sulphuretted hydrogen whitens it, but the colour returns on exposure to the air; metallic zinc and iron have a similar action. By peroxide of mercury it is decomposed into bicyanide of mercury, and an insoluble mixture of oxide and cyanide of iron; by alkalies, into soluble ferrocyanides and peroxide of iron.

In reference to the composition of this compound, it appears from the experiments of Berzelius, that the weight of the iron of the ferrocyanogen is to that combined with it as 3 : 4; from this it may be concluded that its formation is owing to the decomposition of 3 eq. of ferrocyanide of potassium, and 2 eq. of peroxide of iron, into 6 eq. of a potassa salt and into Prussian blue.

$$\left.\begin{array}{l} 3\mathrm{Cfy} + 6\mathrm{K} \\ 2\mathrm{Fe}_2 + 6\mathrm{O} \end{array}\right\} = (3\mathrm{Cfy} + 2\mathrm{Fe}_2) + 6\mathrm{KO}.$$

Prussian blue appears, however, to contain the elements of water, which cannot be separated without the destruction of the compound. If this be the case, it differs from all other ferrocyanides, and must be considered as formed by the direct combination of hydro-ferrocyanic acid and peroxide of iron. Its formula will then be $3\mathrm{CfyH}_2 + 2\mathrm{Fe}_2\mathrm{O}_3$; and the formula given above will represent the hypothetical anhydrous compound.

Prussian blue becomes white in the direct rays of the sun, and cyanogen is evolved; but in the dark it absorbs oxygen and recovers its colour. (Chevreul.) This change of colour in substances dyed with Prussian blue in solar light, arises from a peculiar decomposition; the recovery of the colour is owing to the formation of the so-called basic Prussian blue.

FERROCYANIDES WITH TWO BASIC METALS.

When concentrated solutions of the salts of baryta, strontia, lime, magnesia, protoxide of iron, protoxide of manganese, copper, &c. are added to a solution of the ferrocyanide of potassium, white bulky, frequently crystalline, precipitates are formed, which arise from the replacement of 1 eq. of potassium by 1 eq. of the other metal. Thus, for example, chloride of calcium gives, with the ferrocyanide of potassium, chloride of potassium, and the ferrocyanide of potassium and calcium, $CaCl + K_2Cfy = KCl + \left.\begin{matrix} K \\ Ca \end{matrix}\right\} Cfy$. These double ferrocyanides which contain an alkaline metal, although with difficulty, are nevertheless soluble in water; they contain water of crystallization; when dried at a high temperature they glow with a brilliant light, and cyanate of potassa is formed. (Campbell.)

Ferrocyanide of Potassium and Iron.—This compound is obtained in the form of a bluish-white precipitate when a salt of the protoxide of iron is added to a solution of the ferrocyanide of potassium. By the action of chlorine or nitric acid 3 eq. of potassium and 1 eq. of iron are removed from 3 eq. of the compound; Prussian blue is left. Exposed to the air it absorbs oxygen, and becomes blue; when washed, the ferrocyanide of potassium is dissolved, and after all soluble salts are removed the following compound is left.

Basic Sesqui-ferrocyanide of Iron.—By continued washing the preceding salt dissolves, without leaving any residue of oxide of iron, to a beautiful deep blue solution, which may be again evaporated to dryness without decomposition. The addition of any salt causes the separation of the compound; the precipitate may be redissolved in pure water, and is not thrown down by alcohol. Two eq. ferrocyanide of potassium and iron contain 1 eq. of ferrocyanide of potassium and 3 eq. of ferrocyanide of iron ($6Fe + 3Cfy$); of these 6 eq. of iron, 2 are converted into peroxide by the absorption of oxygen, and the ferrocyanide of potassium is dissolved; so that the soluble blue compound must be represented by the formula $\left\{\begin{matrix} 2Fe_2 \\ Fe_2O_3 \end{matrix}\right\} + 3Cfy$, which corresponds to a compound of 1 eq. of Prussian blue and 1 eq. of peroxide of iron. The formation of this soluble salt is prevented by the presence of a strong acid, which unites with the peroxide of iron, and Prussian blue is left.

Ferrocyanide of Potassium with Sesqui-ferrocyanide of Iron.—The blue precipitate which falls when a salt of the peroxide of iron is added to a solution of ferrocyanide of potassium, always contains, when the iron salt is in excess, variable quantities of the ferrocyanide of potassium; the latter may, by continued washing with water, gradually, although with great difficulty, be removed, which accounts for the constant presence of potassium in the Prussian blue of commerce; it varies from 2 to 9 per cent. If, instead of the salt of peroxide of iron, the ferrocyanide of potassium be in excess, the precipitate is likewise blue, but it is a mixture of Prussian blue with a compound composed of Prussian blue and ferrocyanide of potassium eq. to eq. $2\text{Cfy} + \left\{\begin{matrix} \text{Fe}_2 \\ \text{K} \end{matrix}\right\}$. On washing, the latter is dissolved, giving a deep blue solution, which may be evaporated without decomposition, when it is obtained as a deep blue mass possessed of a strong lustre. It is precipitated by the addition of a salt to its solution, without however losing its solubility in pure water; it is distinguished from the soluble basic Prussian blue by being precipitated from its solution by alcohol.

Ferrocyanide of Potassium with Ferrocyanide of Zinc.—Mosander was the first to point out that the precipitate thrown down by the addition of ferrocyanide of potassium to a zinc salt was not pure ferrocyanide of zinc, but a double compound of the latter with the ferrocyanide of potassium. It is obtained by precipitating any salt of zinc, which is free from iron, by ferrocyanide of potassium, and then washing and drying the precipitate. It is a white, tasteless powder, is insoluble in dilute acids, and contains 2 eq. of ferrocyanogen, 1 eq. potassium, 3 eq. of zinc, and 12 eq. of water $= 2\text{Cfy} + \left\{\begin{matrix} \text{K} \\ 3\text{Zn} \end{matrix}\right\} + 12\text{ aq.}$ A blue tint shows the presence of Prussian blue. It is used in medicine.

FERRID-CYANOGEN.

By treating a solution of ferrocyanide of potassium with chlorine a new compound of potassium is formed, the radical of which contains twice as much cyanogen and iron as exists in ferrocyanogen. We will call it ferrid-cyanogen; it unites with 3 eq. of hydrogen and forms a tribasic acid.

Its formula is $6Cy + 2Fe$; symb. = Cfdy; eq. = 214·34.

The formula of hydro-ferridcyanic acid is . . $Cfdy + H_3$
ferridcyanide of potassium . . $Cfdy + K_3$
ferridcyanide of iron (Prussian blue) $Cfdy + Fe_3$

HYDRO-FERRIDCYANIC ACID.

Prepared by decomposing recently precipitated ferridcyanide of lead by sulphuretted hydrogen, or by the careful addition of dilute sulphuric acid; by filtration a clear yellow solution is obtained, which by careful spontaneous evaporation deposits crystals of a harsh acid taste; but, if heat be used, a deep brown powder is left. The solution readily decomposes on being kept for some time, and a blue crystalline powder is deposited; this change is promoted by heat.

Its formula is $Cfdy + 3H$; eq. = 217·34.

HYDRO-FERRIDCYANIC ACID AND METALLIC OXIDES.

This acid unites with metallic oxides, forming water and a metallic ferridcyanide; of these the compounds with the metals of the alkalies and alkaline earths, as also that corresponding to the peroxide of iron, are soluble in water; all others are insoluble in water. The latter may be prepared by the mutual decomposition of a soluble ferridcyanide and the corresponding metallic salt.

Ferridcyanide of Potassium.—Discovered by L. Gmelin. Prepared by passing a stream of chlorine gas through a solution of ferrocyanide of potassium, until it no longer gives a blue precipitate with salts of the peroxide of iron; the solution is then evaporated, and the crystals obtained by cooling purified from the admixture of chloride of potassium by re-crystallization. Its formation is owing to the decomposition of 2 eq. of ferrocyanide of potassium, $2Cfy + K_4$, by 1 eq. of chlorine into 1 eq. of ferridcyanide, $Cfdy + K_3$, and 1 eq. of chloride of potassium, KCl.

Prop. — Transparent right rhombic prisms of a red colour and high lustre, are anhydrous, permanent in the air, and soluble in 3·8 parts of cold, but more freely in hot water; the crystals burn when held in the flame of a candle with brilliant scintillations; heated in close vessels, cyanogen and nitrogen gases are evolved, a mixture of carburet of iron and ferrocyanide of potassium is the residue. The aqueous solution is decomposed by hydrochloric or hydrosulphuric acid; in the last case, sulphur and cyanide of iron are precipitated, and ferrocyanide of potassium and prussic acid are formed. It is one of the most delicate tests for the protoxide of iron, with which it forms a precipitate similar to Prussian blue; peroxide of iron is not precipitated.

Formula, K_3Cfdy; eq.$=331{\cdot}79$.

Ferridcyanide of Iron.—This compound is likewise sold in commerce as Prussian blue, but it is of a lighter colour and differs from it altogether in constitution. It is prepared by precipitating a solution of the protosulphate of iron by ferridcyanide of potassium, or by a mixture of ferrocyanide of potassium and hypochlorite of soda, to which a certain quantity of hydrochloric acid has been added. In this kind of Prussian blue the three equivalents of potassium of the ferridcyanide of potassium are replaced by 3 eq. of iron. According to the analysis of L. Gmelin, it contains in all 5 eq. of iron, whereas that prepared from ferrocyanide of potassium and salts of peroxide of iron contains 7 eq. of iron; for the same quantity of cyanogen, the weight of iron in the common Prussian blue is to that in the ferridcyanuret as 14 : 15, as is evident from the following formulæ.

$6Cfy+8Fe$, common Prussian blue.

$6Cfy+9Fe$, Prussian blue from ferridcyanuret of potassium.

The peculiarly beautiful Prussian blue sold in commerce under the name of Turnbull's blue, is the ferridcyanide of iron; it is easily recognized by its action on ferrocyanide of potassium, for being boiled in a solution of the latter it is decomposed into ferridcyanide of potassium, which is dissolved, and into an insoluble grey residue of ferrocyanide of iron and ferrocyanide of potassium. (Campbell.)

COBALTO-CYANIDES.

Discovered by L. Gmelin. The cyanuret of cobalt corresponding to the sesqui-oxide Co_2O_3 has not yet been obtained; united with 3 eq. of hydrocyanic acid, it forms the hydro-cobalto-cyanic acid, which is analogous to the hydro-ferridcyanic acid. This acid in its anhydrous state consists of 6 eq. cyanogen, 2 eq. cobalt, and 3 eq. hydrogen; it is a tribasic acid. The symbol of 1 eq. of its radical is Cky; its compounds are as follow:—

$Cky= Cy_6Co_2$=Radical cobalto-cyanogen.
$Cky+H_3$ =Hydro-cobalto-cyanic acid.
$Cky+K_3$ =Cobalto-cyanide of potassium.
$Cky+Pb_3$ =Cobalto-cyanide of lead.
$Cky+Ag_3$ =Cobalto-cyanide of silver.

HYDRO-COBALTO-CYANIC ACID.

Prep.—The cobalto-cyanide of lead is decomposed by sulphuretted hydrogen, and the clear solution, when separated by filtration from the sulphuret of lead, evaporated and allowed to crystallize.

Prop.—Colourless fibrous crystals, of a strong acid taste, deliquescent in a moist air and very soluble in water; the solution decomposes the carbonates with effervescence, and may be boiled and evaporated without change. At a higher temperature, the crystals lose first water and then hydrocyanic acid; a blue residue is left, which at a red heat burns into oxide (Zwenger).

Its formula is $Cky + 3H$; eq. $= 220{\cdot}34$.

Cobalto-cyanide of Potassium.—Discovered by L. Gmelin.

Prep.—The carbonate or pure protoxide of cobalt, or the protocyanide, is gently heated till perfectly dissolved in a caustic solution of potassa, which has been treated with an excess of hydrocyanic acid; the solution evaporated to crystallization, and the crop of reddish-yellow crystals purified by a second crystallization.

Prop. — It crystallizes in nearly colourless or slightly yellow oblique prisms of the same form as the ferridcyanide of potassium; they are anhydrous and fuse to a green fluid. It is more soluble in hot than in cold water; the solution is colourless, without action on vegetable colours; is not decomposed by the hydrochloric, nitric, or sulphuric acids; does not precipitate the salts of iron, but forms a rose-coloured precipitate with those of the protoxide of cobalt.

Its formula is $3K + Cky$; eq. $= 334{\cdot}79$.

Cobalto-cyanide of Lead.— The cobalto-cyanide of potassium causes a slight white precipitate with a solution of acetate of lead, but, by the addition of ammonia, the precipitation is rendered complete. It forms a white granular powder.

Cobalto-cyanide of Silver.—Prepared by mixing the nitrate of silver with the cobalto-cyanide of potassium. It is a white crystalline precipitate, and is soluble in ammonia, with which it forms, by the aid of heat, a double compound, crystallizable in colourless transparent prisms.

CONSTITUTION OF THE FERROCYANIDES ACCORDING TO BERZELIUS.

According to Berzelius, the cyanides form, by uniting with each other, double compounds similar to the double salts, which are produced by the oxacids; in these compounds, therefore, 1 eq. of cyanide of iron is united with 2 eq. of another cyanide, the constitution being such, if the metals be considered united with oxygen, as would be expressed by saying that the oxygen in the protoxide of iron is equal to one-half that in the other metallic oxides. Accordingly, if

Cyanide of iron $= FeCy$.
Hydro-ferrocyanic acid $= FeCy + 2HCy$.
Ferrocyanide of potassium $= FeCy + 2KCy$.
Ferrocyanide of pot. and calcium $= FeCy, 2KCy + FeCy, 2CaCy$.
Prussian blue $= 2Fe_2Cy_3 + 3FeCy$.
Basic Prussian blue $= 2Fe_2Cy_3 + 3FeCy + Fe_2O_3$.
Soluble Prussian blue $= KCy.\ FeCy + 2Fe_2Cy_3.\ 3FeCy$.

COMPOSITION OF FERRIDCYANIDES AND COBALTO-CYANIDES ACCORDING TO BERZELIUS.

These compounds are, according to Berzelius, double cyanides, in which one eq. of sesqui-cyanide of iron or cobalt, analogous in its constitution to the peroxide of iron or cobalt, is united with 3 eq. of another cyanide.

Hydro-ferridcyanic acid is	$Fe_2Cy_3 + 3HCy$.
Ferridcyanide of potassium	$Fe_2Cy_3 + 3KCy$.
Ferridcyanide of iron	$Fe_2Cy_3 + 3FeCy$.
Hydro-cobalto-cyanic acid	$Co_2Cy_3 + 3HCy$.
Cobalto-cyanide of potassium	$Co_2Cy_3 + 3KCy$.

Should the view adopted in this work, although opposed to the opinions of Berzelius, be hereafter shown not to represent the real constitution of these salts, the simplicity in the formulæ, which facilitates their study, particularly in lectures, must nevertheless be considered as a beneficial change.

CONSTITUTION OF THE FERROCYANIDES ACCORDING TO GRAHAM.

The ferrocyanides are formed from a peculiar acid, the eq. of which is triple of that of the hydrocyanic acid; it contains 3 eq.

of cyanogen, which constitutes a radical called prussine in combination with 3 eq. of hyrdogen. This acid is accordingly a tribasic hydracid corresponding to the cyanuric acid; in uniting with a metallic oxide 3 eq. of hydrogen are replaced by their eq. of the metals.

3Cy	$=Pr.$	Prussine.
Hydro-prussic acid . . .	$=Pr+3H.$	
Acid hydro-prusside of iron . .	$=Pr+\left\{\begin{matrix}2H\\Fe\end{matrix}\right\}$	Hydro-ferrocyanic acid.
Prusside of iron and potassium . .	$=Pr+\left\{\begin{matrix}2K\\Fe\end{matrix}\right\}$	Ferrocyanuret of potassium.
Prusside of iron, potassium, and calcium	$=Pr+\left\{\begin{matrix}K\\Ca\\Fe\end{matrix}\right\}$	Mosander's salts.
Prussian blue	$=3Pr+\left\{\begin{matrix}3Fe\\2Fe_2\end{matrix}\right\}$	or $PrFe_3+2PrFe_2$.

This view of the constitution of the ferrocyanides would have the preference to all others, could it offer any explanation why the iron in the ferrocyanide of potassium, for example, cannot be replaced by other metals, which must be the case if it be present as a basic element; in the present state of our knowledge of these double salts it appears, nevertheless, more comprehensive than the views of Berzelius.

CHLORIDE OF CYANOGEN.

Two compounds of chlorine with cyanogen are known, and these are isomeric in their constitution. The one, which at common temperatures is gaseous, was discovered by Gay-Lussac; the other, which is a crystalline solid, by Serullas.

Gaseous Chloride of Cyanogen.—Is formed when chlorine gas is transmitted into hydrated prussic acid, when moist bicyanide of mercury is placed in an atmosphere of chlorine in the dark, or when mellon is heated in dry chlorine gas. This compound which is gaseous at common temperatures, has a most powerful penetrating odour, excites the eyes to a copious flow of tears, becomes solid at 0°, and forms long acicular needles, which fuse at 5° and boil at 10°; but, under a pressure of four atmospheres, it is still liquid at 70°. If the liquid be introduced into glass tubes and hermetically sealed, it is gradually converted into the solid chloride, and regular crystals of the following compound are obtained:—Water dissolves 25, alcohol 100, and ether 50 times its volume of the gas without change. It is decomposed by the alkalies; salts of the protoxide of iron are rendered of a deep green colour when an alkali is added to the mixture. If moistened bicyanide of mercury in chlorine gas be exposed to solar light, a heavy oily liquid of a yellow colour is formed, which is insoluble in water, and has the same odour as the gaseous chloride; the same substance appears to be formed by the action of chlorine upon the fulminate of silver. If it be dissolved in alcohol, and its solution thrown into water, a crystalline substance like camphor is precipitated; on exposing a mixture of moist chlorine and chloride of cyanogen gases to the sun's rays, two other solid compounds appear to be formed. The probable formula of this gas is CyCl.

Solid Chloride of Cyanogen.—Discovered by Serullas. It is formed by exposing dry chlorine gas and anhydrous hydrocyanic acid to the sun's light; hydrochloric acid and the solid chloride, which is deposited in crystals, are formed. It may also be formed by heating sulphocyanide of potassium in a stream of dry chlorine gas. In the pure state it is white, sublimes in long transparent crystals, has a penetrating odour similar to the excrement of mice, and a sweet biting taste; its sp. gr. $=1·32$; fuses at 284°, sublimes at 374°. By digestion in water at a gentle heat, it is decomposed into cyanuric and hydrochloric acids, from which its constitution must be represented by the formula Cy_3Cl_3. It is soluble in absolute alcohol and ether without decomposition.

With dry ammoniacal gas containing chlorine, a white compound, which is not decomposed by water, and sal-ammoniac are formed; its constitution is very imperfectly known.

BROMIDE OF CYANOGEN.

This compound is readily obtained by bringing together in a retort two parts of bicyanide of mercury and one of bromine, by the mixture of which a powerful heat is developed. By applying a gentle heat as soon as the first action is over, the bromide of cyanogen passes over and fills the neck of the retort in the form of white cubic crystals, which are exceedingly volatile, are gaseous at 60°, and are very soluble in water and alcohol. This compound possesses an exceedingly powerful irritating odour, and is very poisonous. Its formula is CyBr.

IODIDE OF CYANOGEN.

Formed by heating dry cyanide of mercury or silver with iodine (Wöhler); most conveniently by heating a mixture of bicyanide of mercury, iodine, and water, in a retort (Mitscherlich), when at a gentle temperature the iodide sublimes, and collects in the neck of the retort as a fine crystalline snow, or in long needles. The crystals have a penetrating odour, which excites a flow of tears, may be dissolved in alcohol, ether, and water without decomposition, and are perfectly volatilized at 100°. Its formula is CyI.

CYANOGEN AND SULPHUR.

Sulpho-cyanogen, Bisulphuret of Cyanogen.—Discovered by Liebig. Prepared by saturating a concentrated solution of a metallic sulphocyanide with chlorine, or by heating it with nitric acid; it falls in the form of a deep yellow, amorphous powder, which retains its colour when dry; is light, porous; is insoluble in water, alcohol, and ether, but is dissolved by strong sulphuric acid from which it is precipitated by water. It is decomposed by nitric acid and by potassium with the aid of heat, giving rise to the formation of the sulphuret, cyanide, and sulphocyanide of potassium; suffers decompositions, which have been but slightly studied, by the action of the alkalies and soluble metallic sulphurets, and is dissolved readily and completely in hydrosulphate of sulphuret of potassium with the evolution of hydrosulphuric acid; from this solution acids throw down a new substance in the form of a white or yellowish-white precipitate. Its decomposition by the action of heat is peculiarly remarkable, the products of its destructive distillation being sulphuret of carbon, sulphur, and the residue mellon, which at a high temperature is decomposed into nitrogen and cyanogen gases. From 4 eq. sulpho-cyanogen, 2 eq. bisulphuret of carbon, 4 eq. sulphur, and a residue of 1 eq. mellon, C_6N_4 are obtained. (See products of the decomposition of sulpho-cyanogen.)

Lassaigne has described in the Ann. de Ch. et Ph. xxxix. as a new compound of cyanogen and sulphur, a substance which he obtained by the action of the perchloride of sulphur upon the bicyanuret of mercury; it occurred as brilliant colourless crystals, which are powerful refractors of light, have a strong penetrating odour, and cause a flow of tears. This substance contains chlorine, the quantity of which has not been determined, 24 per cent. of sulphur and cyanogen; it is dissolved, and at the same time decomposed, by water, and the solution reddens the salts of the peroxide of iron. It is probable that this reputed compound of 2 eq. of cyanogen and 1 eq. sulphur is nothing more than a double compound of the chlorides of cyanogen and sulphur.

Formula, $Cy + 2S$; symb. $= Csy$; eq. $= 58 \cdot 59$.

HYDRO-SULPHOCYANIC ACID.

Discovered by Rink. Occurs in the seeds and blossoms of the Cruciferæ (Senapis, &c.), and in the saliva of man and sheep.

Prep.—By decomposing the basic sulphocyanide of lead by dilute sulphuric acid, care being taken to leave some lead in the solution, which is afterwards separated by sulphuretted hydrogen; or by decomposing sulphocyanide of silver in 10 volumes of water by sulphuretted hydrogen.

Prop.—A colourless fluid of a pure acid taste, which by the action of the air, and on being heated, readily decomposes into a variety of products; one of these deposits itself from the acid as a lemon-yellow, in water insoluble, powder. It cannot exist without water; on treating the aqueous acid with chlorine or nitric acid, it is deprived of hydrogen, and sulpho-cyanogen is precipitated: by a further action cyanic and sulphuric acids are formed, but the former is at once decomposed into carbonic acid and ammonia. It colours the salts of peroxide of iron blood-red, and is not poisonous.

Formula $= Csy + H$; eq. $= 59 \cdot 59$.

HYDRO-SULPHOCYANIC ACID AND AMMONIA.

Sulphocyanide of Ammonium.—By saturating the acid with ammonia and gently evaporating, a semi-fluid saline mass is obtained, which, at a higher temperature, suffers a peculiar decomposition. At first, ammoniacal gas is evolved, then sulphuret of carbon, and at last the protosulphuret of ammonia is sublimed. The residue, when the heat has not been driven too far, consists of melam, or of a mixture of melam with mellon.

Sulphocyanide of ammonium is also formed by adding sulphuret of carbon to alcohol, which has been saturated with ammonia.

Formula $= NH_4 + CyS_2$; eq. $= 75\cdot74$.

METALLIC SULPHOCYANIDES.

The hydro-sulphocyanic acid must be considered as a compound analogous in its constitution to the hydrated cyanic acid, the oxygen of the latter having been replaced by its equivalent of sulphur. Considered as a hydracid, the formula of the hydrated cyanic acid would be

$CyO_2 + H$, corresponding to that of the hydro-sulphocyanic acid, $CyS_2 + H$.

On its being brought into contact with the metallic oxides, the hydrogen is replaced by 1 eq. of the metal. The soluble metallic sulphocyanides may be formed :—by the action of the acid on the metallic oxide, by heating the higher sulphurets of the alkaline metals to redness in cyanogen gas, or by conducting cyanogen gas into their solution, by heating or fusing the soluble metallic cyanides with sulphur, or the insoluble cyanides with the soluble sulphuret.

The soluble metallic sulphocyanides colour the salts of peroxide of iron blood-red; are decomposed, when heated in dry hydrochloric acid gas, into metallic chlorides and anhydrous hydro-sulphocyanic acid, but the latter instantly decomposes into other products. The sulphocyanides of the alkaline metals, when dry, bear a strong heat without decomposition, but, if oxygen be present, they are converted, with the evolution of sulphurous acid, into salts of cyanic and sulphuric acids; those of the heavy metals are decomposed by the red heat into mixtures of metallic sulphurets and mellon, this change being generally accompanied by the evolution of sulphuret of carbon and sulphur; at a higher temperature the residue evolves cyanogen and nitrogen gases in the proportion of 3 : 1. Heated to redness in chlorine gas, they give rise to metallic chlorides, mellon, chlorides of sulphur and cyanogen, and a small quantity of the sulphuret sublimes unchanged; they are most of them soluble in alcohol. The proto-salts of mercury are decomposed by the soluble sulphocyanides into metallic mercury which is deposited, and into the soluble bisulphocyanide. All the soluble sulphocyanides form with the bicyanide of mercury double compounds, which are readily obtained in crystals.

Sulphocyanide of Potassium.—Prep.—Ferrocyanide of potassium, gently roasted to drive off water of crystallization, is mixed in the form of a fine powder with half its weight of flowers of sulphur, and the mixture fused in an iron vessel at a low red heat, until the bubbles of gas which escape through the melted mass inflame in the air and burn with a red light. The mass when cold is dissolved in boiling water, and treated with a solution of carbonate of potassa as long as a turbidity is produced; the whole is then boiled for a quarter of an hour, and the clear liquid separated from the precipitated iron by filtration. On evaporation crystals are obtained, which are separated from the admixture of carbonate of potassa by being redissolved in alcohol.

Prop.—Crystallizes in long striated colourless prisms, which are anhydrous, of a cooling, somewhat biting taste, fuse much below the red heat to a clear liquid; deliquesces in a moist atmosphere, very soluble in hot alcohol, from which it crystallizes on cooling.

Formula, $KCsy$; eq. $= 97{\cdot}74$.

Sulphocyanide of Lead.—Prepared by mixing concentrated solutions of acetate of lead and sulphocyanide of potassium. Forms yellow opaque crystals of a strong lustre, which are decomposed by boiling in water into hydro-sulphocyanic acid and a basic sulphocyanide. Formula is $Csy + Pb$. The basic salt is formed by mixing a solution of sulphocyanide of potassium with subacetate of lead; it is a yellowish-white crystalline insoluble powder.

Its formula is $Csy, Pb + PbO$.

Sulphocyanide of Copper.—Prepared by adding a solution of protosulphate of iron to a mixture of sulphate of copper and sulphocyanide of potassium. It falls as a white granular precipitate, which is insoluble in water.

Formula, $Csy + Cu$.

Sulphocyanide of Silver.—Prepared by precipitating the neutral nitrate of silver by sulphocyanide of potassium. A white curdy precipitate, insoluble in water, but dissolved by ammonia, from which it crystallizes in brilliant white plates.

PRODUCTS OF THE DECOMPOSITION OF CYANOGEN AND ITS COMPOUNDS.

CYANOGEN AND WATER.

A solution of cyanogen in water acquires rapidly in the light, but more slowly in the dark, a brown colour, and a brown flocculent precipitate falls; the solution is then found to contain carbonic acid, prussic acid, ammonia, urea, and oxalate of ammonia (Wöhler); according to the analysis of Pelouze and Richardson, the composition of the brown material may be expressed by NC_2+HO, which denotes a compound of 1 eq. cyanogen and 1 eq. of water. It is readily dissolved by alkalies and acetic acid, but forms with the oxides of the heavy metals insoluble compounds. At a red heat paracyanogen is formed.

The different products, which arise from the reaction of cyanogen and water, are without doubt the results of several perfectly independent decompositions. One eq. of cyanogen and 3 eq. water contain the elements of 1 eq. of anhydrous oxalate of ammonia; 2 eq. cyanogen and 1 eq. water, the elements of 1 eq. of cyanic and 1 eq. of hydrocyanic acid. Carbonate of ammonia is formed from the decomposition of cyanic acid, and three equivalents of water; urea, by the union of cyanic acid with ammonia and water.

CYANOGEN AND AMMONIA.

If cyanogen gas be conducted into liquid ammonia, a decomposition similar to that produced by water ensues, but in a much shorter time. A large quantity of a brown substance, which contains ammonia in chemical combination, is deposited; the soluble products are as above. According to Johnston, the composition of this brown substance may be represented by the formula $C_6N_4H_6O_4$ or $C_6N_3O+NH_3+H_3O_3$, consequently as a hydrated ammoniacal compound of an acid, which contains the same quantity of cyanogen as the cyanuric acid, and may therefore be considered as the protoxide of the radical of the latter acid.

By heating this brown precipitate to redness, paracyanogen, water, and carbonate of ammonia are obtained; this decomposition is readily explained, when it is considered that this product may be considered as a compound of cyanogen (C_4N_2) with ammonia and cyanic acid; the latter of which, by decomposing with 3 eq. water, forms 2 eq. of carbonic acid and 1 eq. of ammonia.

PARACYANOGEN.

Discovered by Johnston. Formed by heating to redness the brown precipitate formed by the decomposition of cyanogen with water or ammonia; left in small quantity on decomposing bicyanuret of mercury in a retort by heat. A dark brown powder, insoluble in water; when burnt with oxide of copper it evolves nitrogen and carbonic acid gases in the proportion of 1 : 2 by volume. Is dissolved by concentrated sulphuric acid; dissolved with decomposition by nitric acid; the addition of water renders the solution turbid, and a yellow precipitate falls, the paracyanic acid (Johnston), the properties and constitution of which require an accurate investigation.

PRODUCTS OF THE DECOMPOSITION OF SULPHO-CYANOGEN.

MELLON.

A compound radical; discovered by Liebig. When dry sulphocyanogen is heated in a retort to redness, it is decomposed into sulphuret of carbon, sulphur, and mellon; 4 eq. sulphocyanogen, $C_8N_4S_8$, yield 4 eq. sulphur S_4, 2 eq. bisulphuret of carbon C_2S_4, and 1 eq. mellon C_6N_4. This substance is also left mixed with chloride of potassium by the decomposition of sulphocyanide of potassium in chlorine gas; also by exposing melam, ammeline, and ammelide to a red heat.

Prop.—A lemon-yellow powder, insoluble in water, alcohol, and dilute hydrochloric and sulphuric acids, but soluble with decomposition in nitric acid and the caustic fixed alkalies; is decomposed by a strong red heat into 3 volumes cyanogen and 1 volume of nitrogen gas; unites directly with potassium with the production of light to the mellonide of potassium, with hydrogen to hydromellonic acid; decomposes the iodide, bromide, and sulphocyanide of potassium, on being fused with them, with the evolution of iodine, bromine, and sulphocyanogen. Its compounds with the other metals are not known.

Its formula is C_6N_4; eq. $= 93{\cdot}32$.

HYDROMELLONIC ACID.

Discovered by L. Gmelin. Prepared by dissolving mellonide of potassium in boiling water, and adding to the solution hydrochloric, sulphuric, or nitric acid. A dirty white gelatinous precipitate which dries to a yellow powder, the hydrated hydromellonic acid. It is slightly soluble in cold, more freely in hot water, has a slightly acid reaction, and is not decomposed by hydrochloric and nitric acids.

Formula, C_6N_4+H; eq. $=94{\cdot}32$.

HYDROMELLONIC ACID AND METALLIC OXIDES.

The hydromellonic acid is decomposed by metallic oxides into a metallic mellonide and water; it decomposes the carbonates both in the dry state and in solution, and the iodides and bromides on fusion. Its compounds with the alkaline metallic oxides and with the earths are insoluble in water.

Mellonide of Potassium.—Prepared by fusing sulphocyanide of potassium in a porcelain crucible at a red heat, and adding mellon as long as an evolution of sulphuret of carbon and sulphur is remarked. A brown opaque glassy mass is obtained, which dissolved in boiling water yields, as the solution cools, hydrated crystals of mellonide of potassium. It may also be formed by fusing 5 parts of chloride of antimony (butter of antimony) with 8 parts of sulphocyanide of potassium, and removing by boiling water the soluble portions of the residue after the escape of the sulphur and the sulphuret of carbon. It is also formed as a secondary product in the process for the preparation of the sulphocyanide of potassium; it is present in the solution in small, but in the residue in larger quantity, from which it may be removed by boiling water.

Prop.—Crystallizes from water in colourless fine needles, which unite into dense flakes; a concentrated solution congeals to a soft white mass, which is with difficulty dissolved by cold water; the crystals contain water of crystallization, which they lose at a high temperature; they then fuse without loss of weight to a clear yellow glass. The solution is tasteless, and precipitates all earthy and metallic salts.

By fusing sulphocyanide of potassium with mellon, the sulphocyanogen is liberated, and is instantly decomposed by the high temperature into sulphuret of carbon, sulphur, and mellon. By fusing 1 eq. chloride of antimony with 4 eq. sulphocyanide of potassium, there are formed 3 eq. chloride of potassium $3KCl$, 1 eq. sulphuret of antimony Sb_2S_3, 2 eq. sulphuret of carbon $2CS_2$, 1 eq. mellonide of potassium KC_6N_4, and 1 eq. of free sulphur. By fusing ferrocyanide of potassium with sulphur, the sulphocyanide of potassium and sulphocyanide of iron are formed; 4 eq. of the latter decompose into 4 eq. sulphuret of iron $4FeS$, 2 eq. sulphuret of carbon $2CS_2$, and 1 eq. of mellon, which as soon as it is formed decomposes 1 eq. of sulphocyanide of potassium into mellonide of potassium and sulphocyanogen; the latter is further decomposed into sulphur, sulphuret of carbon, and mellon.

Formula, $K + C_6N_4$; eq. $= 132{\cdot}47$.

PRODUCTS OF THE DECOMPOSITION OF MELLON.

CYANILIC ACID.

By a long-continued boiling of mellon in dilute nitric acid, a solution is effected with the evolution of gaseous products, and the liquid yields on evaporation colourless, transparent, octohedral crystals; by resolution in hot water, hydrated cyanilic acid in soft tabular crystals of a mother-of-pearl lustre are obtained. This acid has the same composition as the crystalline cyanuric acid; contains, like the latter, 4 eq. water of crystallization, which it loses at 212°, when it becomes opaque and falls to a white powder. By the destructive distillation it is converted into hydrated cyanic acid; by solution in sulphuric acid and caustic potassa into cyanuric acid. This acid has been but little examined. Its formation admits of explanation on the supposition that the elements of 1 eq. of mellon and 3 eq. of water give rise to 1 eq. cyanilic acid and 1 eq. ammonia, and the latter is in point of fact found combined with the nitric acid; according to this, its formation ought not to be dependent on the use of nitric acid alone.

MELLON AND POTASSA.

On boiling mellon with potassa, the former is dissolved with the evolution of ammonia, and on evaporating the solution a very soluble salt of potassa crystallizes in long needles. If the warm solution be treated with acetic acid, a compound containing potassa is precipitated in brilliant crystalline plates; by dissolving these in nitric acid a substance is formed, which is free from potassa, and may be obtained in brilliant and transparent acicular crystals; it gives with salts of silver a white precipitate, which contains 58·8 per cent. of silver, and is not soluble in dilute nitric acid.

HYDRO-PERSULPHOCYANIC ACID.

Product of the decomposition of hydro-sulphocyanic acid. On fusing sulphocyanide of potassium in a stream of dry hydrochloric acid gas, hydro-sulphocyanic acid is separated, but at the same time decomposes into bisulphuret of carbon, hydrocyanic acid, and a yellow substance which is insoluble in water. If this decomposition be conducted in a retort, its neck will be found coated with this yellow or red solid material in large quantity; it is soluble in hot alcohol, from which it is deposited on cooling in the form of a pale yellow crystalline mass, which is slightly soluble in water. The composition of this substance may be represented by the formula $CyS_3 + H$, according to which it contains 1 eq. more of sulphur than the hydro-sulphocyanic acid; it is readily dissolved by the alkalies, and forms, with the other metallic oxides, peculiar and usually insoluble compounds (Woskresensky).

MELAM.

A product of the decomposition of sulphocyanide of ammonium. Discovered by Liebig. When the sulphocyanide of ammonium, or a mixture of 2 parts of sal-ammoniac and 1 of sulphocyanide of potassium are heated to the point of fusion of the latter, the sulphocyanide of ammonium is decomposed into three gaseous and one solid product. The former are ammonia, hydro-sulphuric acid, and the sulphuret of carbon; the latter is melam, which is left in the retort mixed with chloride of potassium, and is separated from it by washing with water.

Prop.—A white amorphous powder; insoluble in water, alcohol, and ether, but dissolved by hot potassa, by which a part of it is decomposed, but another portion is again deposited unchanged as the solution cools; it is also soluble in hot concentrated sulphuric and nitric acids, from which alcohol and water throw down ammelide. If the solution in these strong acids be boiled for some time, it is completely converted into cyanuric acid and ammonia; 1 eq. of melam and 12 eq. water contain the elements of 2 eq. of cyanuric acid and 5 eq. ammonia. It is dissolved in hydrochloric and dilute nitric acids and potassa with the formation of ammeline and melamine; fused with hydrate of potassa, ammonia is evolved, and cyanate of potassa produced; and with potassium the mellonide of potassium is formed. When heated, it decomposes into mellon and ammonia.

Explanations.—On heating 8 eq. of sulphocyanide of ammonium, they are decomposed into 1 eq. melam, 10 eq. ammonia, 4 eq. sulphuret of carbon, and 8 eq. hydrosulphuric acid; 1 eq. melam on being fused with 6 eq. hydrate of potassa, gives rise, by the addition of the elements of 6 eq. of water, to 6 eq. of cyanate of potassa and 5 eq. ammonia. By a long-continued application of heat to melam in caustic potassa, it is decomposed together with 2 eq. water into 1 eq. melamine and 1 eq. ammeline. Melam is converted into ammelide by the addition of the elements of 6 eq. water, which form 1 eq. ammelide and 2 eq. ammonia.

Its formula is $C_{12}N_{11}H_9$; eq. = 238·09.

MELAMINE.

A saline base: discovered by Liebig. A product of the decomposition of melam by alkalies and dilute acids.

Prep.—The residue left from the distillation of 1 part of sulphocyanide of potassium and 2 parts of sal-ammoniac (raw melam) is boiled, after the removal of the chloride of potassium, with a solution of 1 part of hydrate of potassa in 20 parts of water, till the whole is dissolved, and the solution is perfectly clear; it is then gently evaporated till brilliant crystalline scales are observed, when it is allowed to cool and the whole of the melamine is deposited; it is purified by a second crystallization.

Prop.—Crystallizes in pretty large colourless or slightly yellow rhombic octohedrons; they are transparent, anhydrous, sparingly soluble in cold, but pretty freely though slowly in boiling water, unchanged by the air, and insoluble in alcohol and ether. The aqueous solution has no action on vegetable colour, and is of a slightly bitter taste. It fuses when heated, and sublimes principally unchanged, but a small quantity is decomposed into mellon and ammonia. It is decomposed by concentrated nitric and sulphuric acid, with the aid of heat, into ammonia and ammelide or ammeline; fused with hydrate of potassa, the elements of 3 eq. of water add themselves to its constituents and form 6 eq. ammonia, which are evolved, and 3 eq. cyanate of potassa are left.

Its formula is $C_6N_6H_6$; eq. = 121·62.

MELAMINE AND ACIDS.

Melamine combines with dilute acids to crystallizable salts, all of which, with the exception of the double salts, have an acid reaction. The sulphate, nitrate, phosphate, and oxalate are less soluble than melamine itself; the acetate and formiate of melamine are very soluble; it precipitates magnesia from the hot solutions of its salts, owing to the formation of a double salt; the same occurs with all salts, the base of which is an oxide of a heavy metal. Melamine combines directly with the anhydrous hydracids; all its salts with the oxacids correspond to the ammoniacal salt in containing an equivalent of water, without which they cannot exist; it forms double basic salts, in which this equivalent of water is replaced by a metallic oxide.

AMMELINE.

A saline base; discovered by Liebig. A product of the decomposition of melam and melamine by acids and alkalies.

Prep.—The alkaline solution, from which the melamine is formed from the decomposition of melam by the caustic potassa, contains ammeline dissolved in the potassa; it is completely precipitated by neutralizing the solution with acetic acid. The white gelatinous precipitate formed is added to dilute nitric acid as long as it is dissolved, and the solution on evaporation yields crystals of pure nitrate of ammeline; this should be redissolved in very dilute nitric acid, the ammeline precipitated by carbonate of ammonia, and should then be well washed and dried. The substance may also be obtained by dissolving melam in dilute boiling hydrochloric acid, and evaporating when the hydrochlorates of ammeline and melamine crystallize; the crystals are to be dissolved in pure water and precipitated by ammonia. The liquid which drains from the precipitate, as well as the water used in washing, contains melamine, which by evaporation may be obtained as hydrochlorate.

Prop.—A brilliant white precipitate which consists of very fine needles of a silky lustre; it is insoluble in alcohol and ether, but dissolves in caustic alkalies, yields when distilled alone a crystalline sublimate and ammonia, with a residue of pure mellon, is soluble by acids with which it forms crystallizable salts. By long-continued boiling in dilute acids, or on being dissolved in concentrated sulphuric acid, it is decomposed by the addition of 1 eq. of water into ammonia and ammelide. By fusion with caustic potassa, 1 eq. of water is decomposed, and it is converted into ammonia and cyanate of potassa.

Its formula is $C_6N_5H_5O_2$; eq. $= 128{\cdot}47$.

AMMELINE AND ACIDS.

Ammeline is a weak saline base, and forms only with the strong, and not with the organic acids, crystallizable salts which have an acid reaction, and are partially decomposed by water with the deposition of ammeline. By adding a solution of the nitrate of ammeline to the salts of several heavy metals, a crystalline precipitate is formed, which is a basic double salt, composed of 1 eq. of acid, 1 eq. of ammeline, and 1 eq. of metallic oxide. The salts of ammeline with the oxacids contain like the ammonia salts 1 eq. of water, without which they cannot exist; the double salts are anhydrous.

Nitrate of ammeline crystallizes in large broad plates, or in long quadrangular prisms; when heated it fuses, and ammelide is left as a residue, while nitric acid and the products of the decomposition of nitrate of ammonia are evolved.

AMMELIDE.

Discovered by Liebig. A product of the decomposition of melam, melamine, and ammeline by concentrated acids. Melam, melamine, or ammeline is dissolved in concentrated sulphuric acid, the solution mixed with alcohol, and the precipitate formed washed with cold water until all acid is removed. It may be purified by re-solution in dilute nitric acid, and precipitation by carbonate of ammonia.

Prop.—A white powder, insoluble in water, alcohol, and ether, but soluble in alkalies and strong acids, forming with the nitric acid a crystalline compound which is decomposed by water; by continued boiling in dilute nitric or sulphuric acid it is entirely decomposed into cyanuric acid and ammonia.

Formula, $C_{12}N_9H_9O_6$; eq. $= 257{\cdot}79$.

THEORY OF THE COMPOSITION OF MELAMINE, AMMELINE, AND AMMELIDE.

The following attempt has been made to give a satisfactory explanation of the basic qualities of melamine and ammeline, and of their connection with ammelide and cyanuric acid. It is assumed that these substances contain the same radical as cyanuric acid, together with a compound of nitrogen and hydrogen, which is composed of equal volumes of these elements, and which we suppose to be denoted by the symbol $2M = HN$; the compounds may then be represented in the following form :—

Cyanuric acid . . .	$Cy_3O_6 + H_3$.
Melamine . . .	$Cy_3M_6 + H_3$.
Ammeline . . .	$Cy_3M_4O_2 + H_3$.
Ammelide . . .	$Cy_3M_3O_3 + H_3$.
Cyanuric acid . . .	$Cy_3O_3O_3 + H_3$.

The cyanuric acid is, as may be seen, both the commencement and termination of the series; in melamine, the 6 eq. of oxygen are replaced by 6M (N_3H_3), and in ammeline 4 eq. by 4M; both of them are saline bases. The ammelide has no basic properties, and in it one half of the oxygen of the cyanuric acid is replaced by 3M, and by the further removal of all M cyanuric acid is again produced. The basic properties of these bodies decrease as the quantity of oyxgen which combines with the radical is increased. The cyanuric acid may be compared with the phosphoric acid, and melamine with phosphuretted hydrogen or ammonia; ammeline and melamine enter into direct combination with the hydracids and without the intervention of water, but with the oxacids only by the intervention of 1 eq. water, which must be in the same state of combination as in the ammoniacal salts.

CYANOGEN AND HYDROSULPHURIC ACID.

Two compounds of cyanogen and hydrosulphuric acid are known, neither of which are formed when the gases are mixed in a dry state, but are generated by the direct combination of the gases when water is present. The one discovered by Gay-Lussac is obtained by mixing one volume of cyanogen with one and a half volume of sulphuretted hydrogen, a small quantity of water being present; both the gases are absorbed by the water, and on evaporation it deposits long yellow acicular crystals, a solution of which is not precipitated by salts of lead. The other compound was discovered by Wöhler. It is prepared by conducting sulphuretted hydrogen into a saturated solution of cyanogen in alcohol, by which the latter is rendered yellow, and on being artificially cooled deposits this compound of cyanogen and sulphuretted hydrogen in bright orange-red crystals. Insoluble in cold, slightly soluble in boiling water. Very soluble in hot alcohol, from which it may again be obtained in crystals; soluble by alkalies in the cold, and precipitated unchanged from the solution by acids; but on the application of heat a mixture of a metallic sulphuret and a sulphocyanide is formed; its solution precipitates salts of silver, lead, and copper; the compound with the first of these metals is decomposed when gently heated into sulphuret of silver and free cyanogen gas. Its formula is $Cy_3S_6H_6 + aq$.

HYDRO-SULPHOCYANIC ACID AND HYDROSULPHURIC ACID.

Discovered by Zeise. Prepared by saturating 1 volume of absolute alcohol at the temperature of 50° with ammoniacal gas, and adding to the solution a mixture of 0·16 vol. of bisulphuret of carbon, and 0·4 vol. of alcohol; the whole should be placed in a well-stopped glass vessel, which is kept perfectly full at the temperature of 60°. Two products are thus produced, of which the one is a compound of ammonia with an acid formed of sulphuret of carbon and sulphuretted hydrogen; this ammoniacal salt separates in the course of some hours as a crystalline deposite, and the residual liquid contains another ammoniacal salt, the acid of which may be considered as a compound of hydro-sulphocyanic acid and hydrosulphuric acid. This salt is also deposited in a crystalline form when the solution is strongly cooled. By decomposing this ammoniacal salt by hydrochloric acid, an oily substance is obtained, which is the acid of the salt; it is rapidly decomposed by water.

HYPOTHETICAL COMPOUNDS OF CYANOGEN AND CARBONIC OXIDE.

Under these compounds the uric acid and the products of its decomposition are described. These substances are distinctly separated from all known bodies by their chemical relations; an explanation of their formation can only be developed by making certain hypotheses, of which the assumption that they contain cyanogen and carbonic oxide is a deduction drawn from their analyses. The compounds belonging to this group are urile, uric acid, alloxan, alloxantine, and uramile.

The urile, or urilic acid, which may from its composition be also called the cyan-oxalic acid, is an hypothetical compound of nitrogen, carbon, and oxygen, according to the formula $C_8N_2O_4$; it may be considered as a compound of cyanogen and carbonic oxide $2Cy + 4CO$, or as oxalic acid, in which the oxygen which unites with the radical, carbonic oxide, has been replaced by its eq. of cyanogen.

$C_2O_2 + O$ . .	Oxalic acid.
$2(C_2O_2+Cy)$ . .	Cyan-oxalic acid.

If this acid be represented by the symbol Ul, the compounds are represented by the formula :—

Rational formulæ.			Empirical formulæ.
2Ul+1 eq. urea .	=Uric acid .	=	$C_{10}N_4H_4O_6$.
$2Ul+O_2+4$ aq. .	=Alloxan .	=	$C_8\ N_2H_4O_{10}$.
2Ul+O +5 aq. .	=Alloxantine .	=	$C_8\ N_2H_5O_{10}$.
2Ul+1 eq. Amm.+2aq.	=Uramile .	=	$C_8\ N_3H_5O_6$.

URIC ACID.

Discovered by Scheele; first pointed out as existing in the excrement of snakes by Vauquelin, in the excrement of silkworms by Brugnatelli, and in cantharides by Robiquet. Is a product of secretion of all carnivorous animals, of birds, and of many insects; is deposited from human urine generally in combination with ammonia, as it cools, as a yellow or brownish powder; the stone-like concretions in the joints of persons labouring under gout contain uric acid in combination with soda or ammonia; it is the basis of most calcareous deposits in the human bladder. The semi-fluid urine of serpents and birds is principally composed of urate of ammonia. The guano (the decomposed excrement of aquatic birds, which covers the surface of many of the smaller islands of the South Sea, and is used as manure,) is also composed in greater part of urate of ammonia.

Prep.—Urinary calculi, or the white chalk-like excrement of serpents, is reduced to a fine powder and dissolved in a solution of caustic potassa by boiling; the solution is treated with hydrochloric acid in excess, boiled for one quarter of an hour, and the precipitate well washed. It is obtained perfectly pure by decomposing a saturated boiling solution of urate of potassa by hydrochloric acid.

Prop.—Crystallizes in fine scales of a brilliant white colour and silky lustre, is tasteless and inodorous, heavier than water, almost insoluble in cold, slightly soluble, in small quantity, in boiling water; the solution reddens feebly the vegetable colours. It is dissolved by concentrated sulphuric acid, from which it is precipitated by water; in strong hydrochloric acid it is somewhat more soluble than in pure water. Exposed to the destructive distillation, the products of the decomposition of urea are obtained, namely, urea, cyanuric acid, and cyamelide (the insoluble cyanuric acid); also, hydrocyanic acid, a little carbonate of ammonia, and, as a residue, a brown carbonaceous substance which is rich in nitrogen. In this decomposition the hydrated cyanic acid in combination with ammonia is deposited in the neck of the retort as urea. Dissolves in dilute nitric acid with the evolution of equal volumes of pure carbonic acid and nitrogen; the solution contains alloxan, alloxantine, parabanic acid, and ammonia; evaporated and treated with ammonia in excess, it acquires a purple-red colour, a test by which uric acid may be recognized. Fused with hydrate of potassa, carbonic acid, and cyanate of potassa, and cyanide of potassium are obtained; boiled with peroxide of lead in water, it is decomposed into allantoine and oxalic acid, and urea is separated. Is insoluble in ether and alcohol. With sulphuric acid it forms a crystalline compound (Fritzsche).

Its formula is $C_{10}N_4H_4O_6$, or $2Ul + (C_2O_2 + 2NH_2)$.

The latter formula represents uric acid as a compound of urile or cyanoxalic acid with urea; and there is every reason to believe that it contains urea ready formed. In addition to the evidence arising from the action of heat upon it, as well as from the products of its oxidation by peroxide of lead, as above described, Gregory has shown that when uric acid is acted on by permanganate of potash, urea is found among the products. As urea is never *formed* by oxidation, and moreover, according to Gregory, resists the oxidizing agency of the permanganate, we can hardly avoid the conclusion that urea exists as such in uric acid. This would render the existence of the supposed radical urile or cyanoxalic acid, $C_8N_2O_4$, or $2(C_2O_2 + Cy)$, almost a matter of certainty.

URIC ACID AND THE METALLIC OXIDES.

The uric acid appears to unite with the metallic oxides without, as in the other acids, the separation of an eq. of water; its salts, with the fixed alkalies and alkaline earths, are sparingly dissolved by cold, but more freely by boiling water; with ammonia and the other oxides, insoluble compounds, generally of a white colour, are formed. All urates are decomposed by other acids, even by acetic acid; the uric acid is at first separated as a bulky gelatinous mass of hydrated acid, but it shortly afterwards changes into a fine crystalline powder, which is anhydrous.

Urate of Potassa.—Impure urate of ammonia (the excrement of serpents) is dissolved by boiling in a dilute solution of caustic potassa; and the clear liquid, obtained by separating the insoluble portions by filtration, is evaporated. On cooling, the urate of potassa separates as a white crystalline mass, which, when washed by cold water and dried, yields a powder composed of fine acicular crystals of a silky lustre; these crystals are very sparingly soluble in cold water, and the alkaline reaction is scarcely perceptible. Uric acid is more soluble in carbonate of potassa than in pure water; and one half of the carbonate is decomposed.

Urate of Soda.—The action of uric acid upon pure and carbonate of soda is the same as above described for potassa; this salt may also be formed by boiling uric acid in a solution of borax; it is the principal constituent of gouty concretions (Wollaston).

ALLANTOINE.

Hist.—Frequently called allantoic acid. Occurs ready formed in the allantoic fluid of the cow (Vauquelin and Buniva); it is formed when uric acid is boiled in water with peroxide of lead. (Wöhler and Liebig.)

Prep —One part of uric acid is boiled in 20 parts of water, and recently prepared and well-washed peroxide of lead is added in successive portions to the boiling liquid as long as its colour is observed to change. The hot liquid should be filtered, and evaporated until crystals are observed to form upon its surface. The crystals which have deposited when the solution has become quite cold, are purified by recrystallization. Or the allantoic fluid of the cow may be evaporated to one quarter its volume, and the crystals formed on cooling and long standing are purified by animal charcoal.

Prop.—Small transparent and colourless prisms of the right rhombic system, which have a glassy lustre, are tasteless, have no action on vegetable colours, and are soluble in 160 parts of cold, but more freely in hot water. It is soluble in nitric acid, and is decomposed by it when the solution is boiled without the evolution of nitrous fumes. Its composition is such, that it contains the elements of anhydrous oxalate of ammonia minus 3 eq. water; this explains its decomposition by the alkalies, by which it is reduced at the boiling heat into an oxalate and ammonia. Gently heated in concentrated sulphuric acid, it is decomposed into carbonic oxide, carbonic acid, and ammonia; but if a strong heat be rapidly applied, the acid is blackened. It is soluble in caustic and carbonated alkalies by the aid of a gentle heat, and may be again obtained unchanged by crystallization. A solution of allantoine in hot water, to which a little ammonia has been added, produces, with the nitrate of silver, a white precipitate, which contains 43·56 per cent. of oxide of silver, and is composed as represented by the formula, $C_8N_4H_5O_5+AgO$; it consequently contains 2 eq. allantoine, $C_8N_4H_6O_6-1$ eq. water, $HO+1$ eq. oxide of silver.

In the decomposition of uric acid by the peroxide of lead, 2 eq. of oxygen derived from 2 eq. of the peroxide, and 3 eq. water, attach themselves to the constituents of the cyanoxalic acid, by which the latter is decomposed into 2 eq. oxalic acid and 1 eq. allantoine, and the urea is set free.

$$\underline{2PbO+\begin{array}{c}C_4O_4+N_2C_4\\ O_2+H_3O_3\end{array}=\left\{\begin{array}{l}\text{1 eq. cyanoxalic acid}\\ \text{1 eq. urea}\end{array}\right\}}=\text{1 eq. uric acid.}$$
$$\text{2 eq. oxalate of lead}+\text{1 eq. allantoine}+\text{1 eq. urea.}$$

Its formula is $C_4H_3N_2O_3$, or $2Cy+3HO$.

ALLOXAN.

The erythric acid of Brugnatelli; rediscovered by Wöhler and Liebig. One of the products of the decomposition of uric acid by nitric acid. It is best prepared, according to Gregory, by the following method, which is a modification of the original process of Wöhler and Liebig:—Uric acid is gradually added to nitric acid, sp. g. 1·35, by which it is dissolved with effervescence. The action must be gentle, and, if heat be applied, it must be done cautiously. As soon as crystals begin to appear in the warm liquid, no more uric acid is added for the present, and the whole is allowed to cool, when it becomes semi-solid from the separation of the crystals of alloxan. The mass is thrown on a funnel, stopped with a little asbestus, and, when it has ceased to drop, the acid liquor remaining in the crystals is carefully displaced by a little ice-cold water. The crystals are purified by solution in water; avoiding a strong heat, and recrystallization. The acid liquid which has drained from the first crystals is again treated as above with uric acid, and in this way one portion of nitric acid may be made to yield 4 or 5 crops of crystals of alloxan. The mother-liquid finally left is not lost, but yields a large quantity of parabanic acid, oxalurate of ammonia, or murexide, if properly treated. (See those compounds.) By this process Gregory obtains, from 100 parts of uric acid, 65 parts of anhydrous alloxan equal to at least 90 of the hydrated crystals.

Prop.—On the cooling of a warm but not perfectly saturated solution of alloxan, it is obtained in large colourless and transparent crystals of the right prismatic system, and of a strong adamantine lustre; these crystals effloresce rapidly, losing 25 per cent. — 6 eq. water, and are converted when gently warmed, with the loss of water, into anhydrous alloxan. If a hot saturated solution be allowed to crystallize in a warm place, anhydrous alloxan is deposited directly from the solution in oblique prisms, on the extremities of which truncated rhomboidal octohedrons are seen. It is very soluble in water, has a disagreeable odour, and a slightly saline astringent taste, reddens vegetable colours, and causes a purple stain on the skin. Treated with alkalies, alloxanic acid is formed; but on boiling it is decomposed into urea and mesoxalic acid. Heated with peroxide of lead, it is decomposed into urea and carbonate of lead, with which a few traces of oxalate of lead are mixed. When brought into contact with zinc and hydrochloric acid, with chloride of zinc or sulphuretted hydrogen, alloxantine is produced; it is decomposed by free ammonia into mykomelinic acid, by nitric acid into parabanic acid, by sulphuric and hydrochloric acids into alloxantine, by sulphurous acid and ammonia into thionurate of ammonia, with alloxantine and ammonia into murexide. With a protosalt of iron and an alkali, it forms an indigo-blue solution. Does not unite without decomposition with the metallic oxides.

The formation of alloxan and the other products which arise at the same time, is dependent upon two perfectly independent decompositions; namely, upon the conversion of cyanoxalic acid into alloxan, and upon the mutual decomposition of urea and hyponitrous acid. To 1 eq. of cyanoxalic acid are added the elements of 4 eq. water, and 2 eq. oxygen from 1 eq. nitric acid, by which 1 eq. alloxan and 1 eq. hyponitrous acid are formed. The latter combines with the ammonia of the urea, and liberates cyanic acid; the hyponitrite of ammonia is decomposed by heat into nitrogen and water, and the cyanic acid with water is resolved into carbonic acid and ammonia, which unites with the free nitric acid.

$$\begin{array}{ll}
\text{Cyanoxalic acid} = & C_8N_2\quad O_4\\
\text{4 eq. water} & \qquad H_4O_4\\
\text{2 eq. oxygen} & \qquad\quad O_2\\
\hline
\text{1 eq. alloxan} = & C_8N_2H_4O_{10}\\
\text{Urea} & = C_2N_2H_4O_2\\
\text{Hyponitrous acid} = & \quad N\quad O_3\\
\hline
\end{array}$$

$$C_2N_3H_4O_5 = \underset{\text{Ammonia.}}{NH_3} + \underset{\text{Hyponitrous Acid.}}{NO_3} + \underset{\text{Cyanic Acid.}}{C_2NO} + \underset{\text{Water.}}{HO}$$

The hyponitrite of ammonia $NH_3,NO_3 = N_2 + 4HO$; and the cyanic acid C_2NO, with 3 eq. water $2HO$, yields 2 eq. carbonic acid $2CO_2$, and 1 eq. ammonia NH_3. If to the products abovementioned we add alloxantine and parabanic acid, which may be formed by the action of nitric acid on alloxan, the results of this complicated reaction are all clearly accounted for. They are alloxan, alloxantine, parabanic acid, nitrate of ammonia, carbonic acid, and nitrogen. Under certain circumstances nitrate of urea is also formed.

It frequently happens that on dissolving the impure alloxan for the purpose of purifying by a second crystallization, a portion of alloxantine is obtained; it may be easily separated from the alloxan by cold water. (See ALLOXANTINE.)

Alloxanic Acid.—Discovered by Wöhler and Liebig. Produced by the decomposition of alloxan by alkalies. It is prepared by decomposing alloxanate of baryta by sulphuric acid. A strongly acid fluid is obtained, which by gentle evaporation crystallizes in radiated groups of acicular crystals; it is a bibasic acid, dissolves zinc, with the evolution of hydrogen, is unchanged by sulphuretted hydrogen, and precipitates the salts of silver, baryta, and lime. The anhydrous alloxanic acid contains the constituents of alloxan minus 2 eq. water; and the hydrated acid has the same composition as anhydrous alloxan.

Its formula is $C_8N_2H_2O_8 + 2$ eq.

ALLOXANIC ACID AND METALLIC OXIDES.

Alloxanic acid is a bibasic acid, neutralizes the alkalies perfectly, decomposes the carbonates, and forms, when neutralized by ammonia, with the salts of silver, a white precipitate, which, by boiling, becomes first yellow and then black, the change being accompanied by a rapid effervescence; treated with ammonia in excess, it produces white gelatinous precipitates with the salts of lime, strontia, and baryta; but the precipitate is redissolved by a large excess of water, and readily by an acid. The solutions of the neutral alloxanate of lime, strontia, and baryta, become turbid when boiled, the bases are precipitated, and urea and mesoxalic acid are formed.

Alloxanate of Baryta.—Prepared by adding barytic water to an aqueous solution of alloxan at the temperature of 140°; on each addition a white precipitate is formed, but it is redissolved by stirring; the barytic water is added in successive portions till the precipitate is permanent, when the solution is allowed to cool. The mother-liquor separated from the crystals is again to be heated and treated with barytic water as before, and this should be repeated as long as crystals are obtained.

Short transparent needles, or mother-of-pearl scales, which at 212° become milk-white and lose 3 eq. water; at 300° they are anhydrous; they are sparingly soluble in cold, but more freely in hot water; exposed to a red heat they leave a mixture of carbonate of baryta and cyanide of barium.

Its formula is $C_8N_2H_2O_8,2BaO + 8$ aq.

Alloxanate of Silver.—A white insoluble powder, which produces a slight explosion when heated; the residue after being heated to redness yields cyanic acid and metallic silver.

Its formula is $C_8N_2H_2O_8 + 2AgO$.

MESOXALIC ACID.

When a saturated solution of alloxanate of baryta or strontia is heated to the boiling point, a precipitate falls consisting of the carbonate, mesoxalate, and alloxanate of baryta or strontia. The solution, on evaporation, yields a crystalline crust, from which urea is separated by treating it with alcohol, and mesoxalate of baryta remains. If a solution of alloxan be added, drop by drop, to a boiling solution of acetate of lead, a very heavy granular precipitate of mesoxalate of lead is formed, and urea remains as the only other product in the solution. The mesoxalic acid may be obtained by decomposing this lead salt by sulphuric acid; it is a strongly acid solution, reddens vegetable colours, and forms, like the alloxanic acid, on the addition of ammonia, precipitates with the salts of baryta and lime, which are soluble in acids and a large excess of water; it may be boiled and evaporated without change. Its action on the salts of silver is characteristic; it forms with them, after being neutralized by ammonia, a yellow precipitate, which on being gently heated is reduced to the metal with a rapid effervescence. The above-mentioned lead salt yields, on analysis, 80·4 per cent. of oxide of lead; it contains a slight admixture of a substance containing nitrogen, probably cyanate or cyanurate of lead, from which it cannot be perfectly purified. The composition of the lead salt is very probably expressed by the formula $C_3O_4 + 2PbO$, in which case its formation from alloxan and alloxanic acid admits of a ready explanation. From 1 eq. alloxan 1 eq. urea is separated, by which 2 eq. of anhydrous mesoxalic acid is left.

$$\begin{array}{ll} \text{1 eq. alloxan} & = C_8N_2H_4O_{10} \\ -\text{1 eq. urea} & = C_2N_2H_4O_2 \\ \hline = \text{2 eq. mesoxalic acid} & = C_6 \qquad O_8 \end{array}$$

The above-mentioned mesoxalate of baryta contains 56 per cent. of baryta, from which its constitution is probably represented by the formula $C_3O_4 + \left\{ \begin{matrix} BaO \\ HO \end{matrix} \right\}$. Mesoxalic acid is therefore most probably a bibasic acid, and is very remarkable as a new compound of carbon and oxygen.

MYKOMELINIC ACID.

Discovered by Wöhler and Liebig. Product of the decomposition of alloxan by ammonia. It is prepared by heating to 212° a solution of alloxan with an excess of ammonia, then neutralizing with an excess of dilute sulphuric acid and boiling for a few minutes. The mykomelinic acid falls as a yellow gelatinous precipitate, which dries to a yellow porous powder; it is with difficulty dissolved by cold, but more readily by hot water; the solution has a distinctly acid reaction; it decomposes the carbonated alkalies and is easily dissolved by the caustic alkalies, but on being boiled with them is decomposed with the evolution of ammonia; it forms, with the oxide of silver, a yellow compound, which is insoluble in water. It is produced by the decomposition of 1 eq. alloxan and 2 eq. ammonia into 1 eq. mykomelinic acid and 5 eq. water.

Its formula is probably $C_8N_4H_5O_5$.

PARABANIC ACID.

Discovered by Wöhler and Liebig. Product of the decomposition of uric acid and alloxan by nitric acid. Prepared by treating 1 part of uric acid, or 1 part of alloxan, in 8 parts of pretty strong nitric acid, evaporating to the consistence of a syrup, and allowing it to stand for some time, when it yields colourless crystals which may be purified by a second crystallization. It may be obtained in abundance from the mother-liquor of the preparation of alloxan by Gregory's process, if that liquid be heated with an additional quantity of nitric acid.

Prop.—Colourless, transparent, thin, hexagonal prisms; has a strong acid taste, very similar to that of oxalic acid; is very soluble in water, does not effloresce either in the air or in a warm room; fuses if heated, when a portion sublimes unchanged, but another part decomposes with the evolution of hydrocyanic acid. The cold solution neutralized by ammonia produces a white precipitate in the salts of silver, which contains 70·62 per cent. of the oxide; when treated with ammonia it is converted into oxaluric acid.

It is formed by the decomposition of 1 eq. of uric acid, which by the addition of 2 eq. of water and 4 eq. oxygen from the nitric acid, is resolved into 2 eq. carbonic acid, 1 eq. parabanic acid, and 1 eq. urea; the latter is decomposed as before-mentioned by the hyponitrous acid. One eq. alloxan with 2 eq. oxygen is solved into 2 eq. carbonic acid, 4 eq. water, and 1 eq. parabanic acid.

The formula of the crystalline acid is $C_6N_2O_4 + 2$ aq. It is probably a bibasic acid.

OXALURIC ACID.

Discovered by Wöhler and Liebig. Produced by the decomposition of parabanic acid. Prepared by adding dilute sulphuric or hydrochloric acid to a saturated solution of oxalurate of ammonia in hot water, and rapidly cooling the mixture when the oxaluric acid falls as a white crystalline powder; this should be washed with cold water as long as the washing, when neutralized by ammonia, causes with the salts of lime a precipitate which is perfectly redissolved by heat, or by an additional quantity of water. It is a white, or slightly yellow crystalline powder of an acid taste, reddens the vegetable colours, and when neutralized by ammonia, forms with silver salts a white precipitate which is perfectly redissolved by boiling. By boiling in water it is completely decomposed into free oxalic acid and oxalate of urea. The oxaluric acid is formed by the addition of 2 eq. water to the constituents of the parabanic acid. It contains further the elements of 2 equivalents of oxalic acid and 1 eq. urea; it may be considered as uric acid in which the cyanoxalic acid has been replaced by the oxalic acid.

Its formula is $C_6N_2H_3O_7 + aq.$

Oxalurate of Ammonia.—This salt may be formed by heating a solution of parabanic acid with ammonia, or more advantageously by treating a recently prepared solution of uric acid in dilute nitric acid with an excess of ammonia and evaporating. The liquid acquires at first a purple colour, which disappears during the evaporation, and if allowed to cool when arrived at a certain degree of concentration, it deposits radiated groups of hard acicular yellow crystals; they are obtained colourless by charcoal and recrystallization.

The oxalurate of ammonia crystallizes in radiated groups of fine acicular crystals, which have a silky lustre, and are readily dissolved by hot, but with difficulty by cold water; the solution has no reaction on vegetable colours, and may be boiled and evaporated without change; the dry salt loses no weight at 250°, but at a higher temperature it is decomposed with the rapid evolution of hydrocyanic acid. Acids separate from a concentrated solution the oxaluric acid as a crystalline powder.

Its formula is $NH_4O + C_6N_2H_3O_7$.

OXALURIC ACID AND METALLIC OXIDES.

The oxaluric acid forms with the alkalies very soluble, but with the alkaline earth sparingly soluble salts. If concentrated solutions of oxalurate of ammonia, chloride of calcium or barium be mixed with each other, after standing some time, brilliant transparent scales or needles of oxalurate of baryta or lime will be deposited; a solution of the latter in water when treated with an excess of ammonia gives a basic salt in the form of a transparent gelatinous precipitate, which is redissolved by a large quantity of water.

Oxalurate of Silver.—This salt is obtained by mixing boiling solutions of oxalurate of ammonia and nitrate of silver, and is deposited as the solution cools in long anhydrous needles of a silky lustre; these are decomposed at a high temperature without explosion.

Its formula is $AgO + C_6N_2H_3O_7$.

THIONURIC ACID.

A bibasic acid. Discovered by Wöhler and Liebig. Is formed by the action of sulphurous acid on alloxan. It is prepared by decomposing the thionurate of lead by hydrosulphuric acid. A white crystalline mass, is permanent in the air, and readily dissolved by water; of an acid taste, reddens vegetable blues strongly; its saturated solution, when heated to the boiling point, congeals to a semifluid crystalline mass of uramile, and the fluid when this has deposited is found to contain free sulphuric acid. The thionuric acid contains the elements of 1 eq. alloxan, 1 eq. ammonia, and 2 eq. sulphurous acid; the uramile may be considered as a compound of ammonia with alloxan minus 2 eq. oxygen, or of cyanoxalic acid with 1 eq. ammonia and 2 eq. water. On heating the solution of thionuric acid 2 eq. oxygen are given by 1 eq. alloxan to the 2 eq. of sulphurous acid, which is thus converted into sulphuric acid, while the elements of cyanoxalic acid, ammonia, and water combine to form uramile.

Its formula is $C_8N_3H_7O_{14}S_2$, or $C_8N_2H_4O_{10} + NH_3 + 2SO_2$, that is, 1 eq. alloxan, 1 eq. ammonia, and 2 eq. sulphurous acid. But as it contains 2 eq. of water, capable of being replaced by bases, the true formula probably is $(C_8N_3H_5O_8, 2SO_2) + 2HO$.

Thionurate of Ammonia.—*Prep.*—A cold solution of alloxan is mixed with an excess of an aqueous solution of sulphite of ammonia; the mixture is then treated with pure ammonia in excess, and boiled for five minutes. As the solution cools, the thionurate of ammonia crystallizes, and may then be washed and dried.

Prop.—Quadrangular scales of a strong mother-of-pearl lustre, which lose at 212° 6 per cent. = 2 eq. water, and acquire a pink colour; sparingly soluble in cold, freely in boiling water. If a solution of this salt be heated with a dilute mineral acid, it suffers the same decomposition as the free acid; mixed with nitrate of silver, the metal is after some time deposited of a brilliant metallic lustre. If to a solution of the salt a smaller quantity of sulphuric acid be added than is sufficient to neutralize the ammonia which it contains, and then evaporated in a water-bath, a soft white thionurate of ammonia in thin acicular crystals is obtained, which when boiled is decomposed into ammonia and uramilic acid.

Formula of thionurate of ammonia $(C_8N_3H_5O_8,2SO_2) + 2NH_4O + 2$ aq.

THIONURIC ACID AND METALLIC OXIDES.

Thionuric acid forms with the alkalies very soluble salts; with the alkaline earths either insoluble or sparingly soluble salts, which are however readily dissolved by dilute acids; they generally are formed of 1 eq. of acid and 2 eq. of the metallic oxide. All these salts evolve sulphurous acid abundantly when treated with concentrated sulphuric acid; when fused with hydrate of potassa, sulphite of potassa is formed.

Thionurate of Lime. — Prepared by mixing a hot solution of thionurate of ammonia with nitrate of lime. It crystallizes in short fine prisms of a silky lustre.

Thionurate of Baryta.—The barytic salt is precipitated even by very dilute solutions of the thionurates in thick gelatinous flakes, which are readily redissolved by acids.

Thionurate of Lead. — A thick gelatinous precipitate, which rapidly changes in warm water to fine short needles of a white colour; on drying they lose water and become pink. Exposed to the destructive distillation they yield urea, together with a peculiar substance which crystallizes in large broad tables.

Thionurate of Zinc.—Small crystalline concretions of a lemon-yellow colour.

URAMILE.

Discovered by Wöhler and Liebig. A product of the decomposition of thionuric acid.

Prep. — A hot saturated solution of thionurate of ammonia is treated with hydrochloric acid till it has a strongly acid reaction, boiled till a slight turbidity is observed, when the whole is soon converted to a semifluid mass. It is obtained in a plume-form aggregation of fine but hard needles, or as a fine porous powder, consisting of fine needles which have a silky lustre, and are permanent in the air, but acquire a pink tint when heated; insoluble in cold, but taken up in small quantity by boiling water; soluble in ammonia and the caustic alkalies in the cold, from which it is precipitated by acids unchanged. Uramile is formed from thionuric acid ($C_8N_3H_5O_8,2SO_2$) by the conversion of the 2 eq. sulphurous acid into sulphuric acid; $C_8N_3H_5O_8,2SO_2 = C_8N_3H_5O_6 + 2SO_3$. When thionuric acid alone is used, the sulphuric acid is set free. When thionurate of ammonia is boiled with an acid, the ammonia is removed by the acid employed, and the thionuric acid, being set free, undergoes the above decomposition. The solution of uramile in ammonia and caustic potassa acquires a purple colour by exposure to the air, and deposits green acicular crystals of a brilliant metallic lustre; if boiled in the caustic potassa, it is decomposed into uramilic acid with the evolution of ammonia. It is soluble in concentrated sulphuric acid, from which it is again precipitated by water; by boiling in dilute acids it suffers the same change as in caustic potassa. By boiling with the oxides of silver and mercury it is converted into murexide, and the oxide is reduced. With concentrated nitric acid it is resolved into alloxan, with the evolution of hyponitrous acid, and the formation of nitrate of ammonia. Uramile may be considered as uric acid, in which the urea is replaced by 1 eq. ammonia and 2 eq. water.

Its formula is $C_8N_3H_5O_6$, or $C_8N_2O_4,NH_3,2HO$; eq. = 144·41.

URAMILIC ACID.

Discovered by Wöhler and Liebig. A product of the decomposition of uramile.

Prep.—A saturated solution of thionurate of ammonia in cold water is added to a small quantity of sulphuric acid, and the mixture evaporated in a water-bath, when the uramilic acid is slowly deposited in transparent prisms of a glassy lustre. If a white amorphous deposite, which is soluble in hot water, be at the same time obtained, it arises from the presence of undecomposed acid thionurate of ammonia; this is again dissolved in water mixed with sulphuric acid, and treated as before.

Prop.—Colourless four-sided prisms, or fine silky needles; is soluble in 6—8 parts of cold, and in 3 parts of boiling water; loses no weight when heated to 212°, but acquires a slightly pink colour; the solution has a feeble acid reaction. It is soluble in concentrated sulphuric acid with effervescence, but without colouring the acid. By boiling in strong nitric acid, a yellow solution is obtained, which yields on evaporation white crystalline and sparingly soluble scales or granular crystals; they are dissolved by alkalies, and again precipitated by acetic acid. In the formation of uramilic acid 2 eq. of uramile lose the elements of 1 eq. of ammonia, which are replaced by 3 eq. of water.

Its formula is $C_{16}N_5H_{10}O_{15}$.

SALTS OF URAMILIC ACID.

The uramilic acid forms with ammonia and the fixed alkalies soluble crystallizable salts; lime and baryta are not thrown down from their saline solution by the free acid; but on the addition of ammonia a white precipitate is formed, which again disappears in a large quantity of water. Uramilate of ammonia produces with nitrate of silver a dense white precipitate, which contains from 63—64 per cent. of silver.

ALLOXANTINE.

First observed by Prout as a product of the decomposition of uric acid by nitric acid; it is also formed by the action of chlorine on uric acid, as likewise from alloxan by the action of deoxidizing agents.

Prep.—From uric acid: one part of uric acid is added to 32 parts of water, which is brought to the boiling point, and then treated with dilute nitric acid in successive portions till a perfect solution is obtained; it should then be evaporated to two-thirds of its volume, when, after standing for some hours, or a day, crystals of alloxantine will be deposited, which should be purified by recrystallization.—*From alloxan:* it is obtained in large quantity by transmitting a stream of hydrosulphuric acid gas through a solution of alloxan, when first sulphur, and then a crystalline mass of alloxantine is deposited; it is separated from the sulphur by solution in hot water, which yields by evaporation and cooling pure crystals of alloxantine. It may also be formed by adding zinc and hydrochloric acid to a solution of alloxan, but here an excess of acid must be carefully avoided; or by boiling alloxan in moderately strong sulphuric acid, when it is deposited as the solution cools. Diluted hydrochloric acid, and even diluted nitric acid, produce the same effect. The latter fact is curious, because stronger nitric acid reconverts alloxantine into alloxan; and also because the conversion of alloxan into alloxantine is a process of deoxidation. The reaction, in this mode of preparation, however, is different from that which occurs when sulphuretted hydrogen is employed. It is explained below for sulphuric acid, and the explanation applies to nitric and hydrochloric acids (Gregory). If a solution of alloxan be exposed to the action of a galvanic battery, oxygen is evolved at the positive electrode, while the negative is covered with a crystalline crust of alloxantine.

Prop.—Short oblique four-sided prisms of the oblique prismatic system, the obtuse angle of the prism being 105°. The crystals are colourless, or have a slightly yellow tint; in an ammoniacal atmosphere they become red, acquire a greenish metallic lustre, and are readily reduced to powder; exposed to 212° they undergo no change of weight, but at 300° lose 15·4 per cent. = 3 eq. water; sparingly soluble in cold, more freely in boiling water. The solution reddens litmus; is converted into alloxan by being warmed with strong nitric acid, or by a solution of chlorine; forms with the salts of silver a black precipitate of metallic silver; it is decomposed by alkalies; barytic water causes a violet-blue precipitate, which is first rendered colourless by heat and then disappears; by adding an excess of baryta to this solution a brilliant white precipitate is formed.

By the action of dilute nitric acid upon uric acid, only 1 eq. of oxygen is taken up by the cyanoxalic acid, and there is formed by the addition of the elements of 5 eq. of water, 1 eq. alloxantine and nitrous acid, which is decomposed by the water into $\frac{1}{2}$ eq. of hyponitrous acid, and $\frac{1}{2}$ eq. nitric acid; the former reacts as described in alloxan upon half of the urea liberated, causing their mutual decomposition, while the other half of the urea combines with the nitric acid to nitrate of urea. In its preparation from alloxan 1 eq. oxygen of the latter is converted, by the hydrogen of the sulphuretted hydrogen, into water, which remains in combination with the other elements. On boiling alloxan with sulphuric acid 2 eq. are decomposed into 1 eq. alloxantine, 3 eq. oxalic acid, 1 eq. ammonia, and 1 eq. cyanic acid; the latter being decomposed, together with 3 eq. water, into carbonic acid and ammonia. If a solution of alloxan, instead of being left in contact with zinc and hydrochloric acid at common temperature, be heated to the boiling point, and kept at that temperature for some time, it deposits, on cooling, yellow granular crystals of a brilliant lustre and sparing solubility in boiling water, and of characters essentially different from alloxantine.

Its formula is $C_8N_2H_5O_{10}$, or $C_8N_2O_4+O+5HO$; eq. = 162·26.

Products of the decomposition of Alloxantine.—If a stream of sulphuretted hydrogen gas be passed through a boiling solution of alloxantine, a further precipitation of sulphur ensues, and the solution acquires a strongly acid reaction; if neutralized by carbonate of ammonia, it deposits on cooling an abundant crop of white silky acicular crystals of an ammoniacal salt, which, when heated to 212° in the air, becomes of a blood-red colour; its composition is represented by the formula $C_8N_3H_7O_8$, and it may therefore be considered to be a compound of cyanoxalic acid with 1 eq. ammonia and 4 eq. water. The acid in this salt, when we attempt to separate it from the ammonia with which it is combined, appears to be decomposed into a variety of new products. It is proposed to call this acid the dialuric acid, since its properties appear to differ from those of the cyanoxalic. It is probable that the dialurate of ammonia may be $C_8N_2H_3O_7+NH_4O$. If this be so, the anhydrous dialuric acid will be $C_8N_2H_3O_7=C_8N_2O_4+3HO$; that is, containing the elements of 1 eq. cyanoxalic acid and 3 eq. water. One of the products of its decomposition is obtained by dissolving the ammoniacal salt in dilute sulphuric or hydrochloric acid, and exposing it to the air for some time; it crystallizes from this solution in hard colourless crystals, which in their chemical properties entirely coincide with alloxantine, but differ from it in their crystalline form; it may be called dimorphous alloxantine. The same substance is formed when uramile or uramilic acid is heated with dilute sulphuric or hydrochloric acid until perfectly decomposed.

If a hot saturated solution of alloxantine be treated with a solution of sal-ammoniac, it instantly acquires a purple-red colour, which disappears after a few moments, while the solution becomes turbid, and deposits brilliant white scales of uramile, which are pink when dried; the same occurs with the acetate, the oxalate, and other ammoniacal salts; the solution contains, after the decomposition, alloxan and free hydrochloric acid. Two eq. alloxantine and 1 eq. ammonia contain the elements of 1 eq. uramile, 1 eq. alloxan, and 4 eq. water. By heating a solution of alloxantine in pure ammonia, the products first formed are uramile and mykomelinate of ammonia, both of which suffer further changes by the continued action of ammonia and the atmospheric air. If a solution of alloxantine in ammonia, which has been prepared in the cold, be spontaneously evaporated by exposure to the air, oxygen is absorbed, and crystals of the oxalurate of ammonia are obtained; 3 eq. alloxantine, 7 eq. oxygen, and 6 eq. ammonia, contain the elements of 4 eq. oxalurate of ammonia and 5 eq. water.

If oxide of silver be heated in a solution of alloxantine, a portion of the former is reduced with effervescence, and the solution contains pure oxalurate of silver. In this reaction 3 eq. oxygen from the oxide of silver decompose 1 eq. alloxantine into 1 eq. water, 2 eq. carbonic acid, and 1 eq. oxaluric acid, which last unites with some undecomposed oxide of silver. Peroxide of mercury is dissolved by alloxantine without effervescence, and the solution appears to contain alloxanate of the protoxide of mercury. A solution of alloxantine by boiling with peroxide of lead is decomposed into urea and carbonate of lead.

MUREXIDE.

The purpurate of ammonia discovered by Prout. *Prep.*—By heating a mixture of equal parts of peroxide of mercury and uramile in 36—40 parts of water, with the addition of an exceedingly small quantity of ammonia; as soon as the liquid has acquired a deep purple colour, it is filtered and allowed to rest, when the murexide crystallizes; or by dissolving uramile by the aid of heat in ammonia, and when the solution has cooled to 160°, alloxan is added until a very slight alkaline reaction is observed. Or a solution of uric acid in dilute nitric acid is evaporated until it acquires a flesh-red colour, when it is allowed to cool to 160°, and is then treated with a dilute aqueous solution of ammonia, till the presence of free ammonia is remarked by the odour; the solution is then diluted with half its volume of boiling water, and allowed to cool. In this method of preparation, it is advisable to test a small quantity of the solution of uric acid from time to time by saturating it with ammonia: if it be rendered turbid by the ammonia, and a red powder falls, a small quantity of nitric acid must be added to the hot solution of the uric acid; but if a yellow slimy precipitate be formed, the solution will only give rise to the formation of murexide after a stream of sulphuretted hydrogen has been transmitted through it. Or a boiling saturated solution of alloxantine in water is treated with ammonia in excess till the precipitated uramile is redissolved, when a solution of alloxan is added, so that only a slight alkaline reaction is left, and the whole is allowed to cool. Or by heating alloxantine with sal-ammoniac or oxalate of ammonia, and after the formation of uramile adding ammonia till the former is redissolved, and then alloxan. Murexide may be formed by a number of other processes, by bringing together many of the products of uric acid with ammonia, with or without the presence of atmospheric air. The easiest and most certain method, which is also the most productive, is the following, proposed by Liebig, and slightly modified by Gregory. Seven grains of hydrated alloxan and 4 grains of alloxantine are dissolved by boiling in 240 grains of water, and the boiling solution added to 80 grains by measure of a cold and strong solution of carbonate of ammonia. This mixture has precisely the proper temperature, and deposits very fine crystals of murexide. The experiment is not so succcessful on a large scale, probably because the liquid, by remaining longer warm, undergoes a partial change. It is best to try first a saturated solution in cold water of carbonate of ammonia. If it do not yield good crystals, add a little water, and try it again, and so on till a solution of the carbonate is obtained which gives a good result. The difficulty is owing to the spontaneous formation of different carbonates by the action of water on the carbonate of the shops; but when a proper solution is obtained the experiment never fails; and is well adapted for the lecture table.

When the oxygen from $1\frac{1}{2}$ eq. of peroxide of mercury is added to 2 eq. uramile, they may give rise to the formation of 1 eq. murexide, 1 eq. alloxanic acid, and 3 eq. water. Alloxan appears to have the same action upon a solution of uramile in ammonia as the peroxide of mercury. One eq. alloxan, 2 eq. alloxantine, and 4 eq. ammonia, contain the elements of 2 eq. murexide and 14 eq. water. The solution of uric acid in dilute nitric acid contains principally alloxantine, urea, and nitrate of ammonia: evaporated until the flesh-red colour appears, a portion of the alloxantine is converted by the action of free nitric acid into alloxan, a portion of which, by a further action, gives rise to parabanic acid. But when alloxan and alloxantine are simultaneously present in a solution, an excess of ammonia produces a deep purple-red liquid from which murexide is deposited. If the solution contain an excess of alloxantine, the crystals of murexide are mixed with uramile; with an excess of alloxan mykomelinate of ammonia is formed, which also falls with the murexide. The parabanic acid present passes, when the solution of uric acid is saturated with ammonia, into oxaluric, which is obtained in crystals of oxalurate of ammonia by evaporating the mother-liquid.

Prop.—Murexide crystallizes in short four-sided prisms, two faces of which, like the upper wings of the cantharides, reflect a green metallic lustre. The crystals are transparent, and by transmitted light are of a garnet-red colour. It forms a brownish-red powder, which, under the polishing steel, acquires a brilliant metallic green colour. It is insoluble in ether and alcohol; sparingly soluble in cold, but more readily in boiling water, on the cooling of which it crystallizes unchanged; insoluble in a saturated solution of carbonate of ammonia, soluble in caustic potassa with a beautiful purple colour, which disappears on the application of heat with the evolution of ammonia. It is decomposed either in the solid state or in solution by all the mineral acids, with the separation of brilliant scales of murexan; the liquid contains ammonia, alloxantine, alloxan, and urea. The instant the murexide is brought into contact with hydrosulphuric acid, it is decomposed into alloxantine, dialuric acid, and murexan, with the separation of sulphur. An equivalent of alloxan, alloxantine, murexan, and urea, together with 2 eq. ammonia, contain the elements of 2 eq. murexide and 11 eq. water.

Its formula is $C_{12}N_5H_6O_8$; eq.$=$197·19.

The above formula has been preferred to one or two others, which may also be deduced from the analyses of murexide by Wöhler and Liebig, because, by adopting it, we can explain, in some cases, the formation and the decomposition of murexide. But the composition of murexide cannot be considered as fully ascertained. Indeed, Gregory has suggested that there are most probably two varieties of murexide, agreeing in aspect, but differing in chemical characters and composition. Thus he found that some specimens do not yield a trace of murexan when acted on by acids, and that murexide sometimes occurs which is very soluble in weak ammonia, while that analysed by Wöhler and Liebig was nearly insoluble, if not quite so, in that liquid. The subject requires careful study, and is of great importance, as the true theory of the formation of murexide must throw light on the formation of those organic colouring matters which are produced, like murexide, by the action of ammonia on colourless substances, such as indigo, litmus, cudbear, &c.

MUREXAN.

The purpuric acid discovered by Prout as the product of the decomposition of murexide. Prepared by dissolving murexide in caustic potassa by the aid of heat, which is applied till the blue colour disappears, when dilute sulphuric acid is added in excess.

Prop.—It falls in crystalline scales of a silky lustre; is insoluble in water and dilute acids, but is taken up by ammonia and the fixed alkalies in the cold without neutralizing them. It is dissolved by concentrated sulphuric acid, from which it is again precipitated unchanged by water. If a solution of murexan in ammonia be exposed to the air, it acquires a purple-red colour, and deposits the brilliant crystals of murexide; with an excess of ammonia the solution again becomes colourless, and is then found to contain oxalurate of ammonia. Two eq. murexan, 1 eq. ammonia, and 3 eq. oxygen, contain the elements of 1 eq. murexide and 3 eq. water; 1 eq. murexan, 3 eq. oxygen, and 1 eq. ammonia are the constituents of 1 eq. oxalurate of ammonia.

Its formula is $C_6N_2H_4O_5$; eq. $= 109 \cdot 02$.

The properties of murexan closely resemble those of uramile, and the difference in their composition in 100 parts is not very great. In addition to the properties above mentioned, Gregory states that murexan, if boiled with water, peroxide of mercury, and a little ammonia, yields murexide just as uramile does. It is possible that these two substances may be essentially the same.

APPENDIX TO THE COMPOUNDS OF URIC ACID.

Uric Oxide, or Xanthic Oxide.—A rare constituent of urinary calculi; first discovered by Marcet.

Prep.—Urinary calculi, which contain this ingredient, are dissolved in caustic potassa and the solution saturated with carbonic acid, when the uric oxide is precipitated.

Prop.—A white precipitate; when dried, it forms a pale yellow hard mass, which acquires a waxy lustre by friction: it is dissolved by the pure and carbonated alkalies; in small quantity by hot water, hydrochloric and oxalic acids. It is soluble in concentrated sulphuric acid with a yellow colour; no precipitation is caused by the addition of water to the solution. It is dissolved in nitric acid without effervescence; on evaporating to dryness, a lemon yellow residue is left, which is not reddened by ammonia, is partially soluble in water, but perfectly and easily in potassa; the solution has a light reddish-yellow colour, and leaves on evaporation a red residue. Exposed to the destructive distillation, it evolves an odour of urine, hydrocyanic acid, and carbonate of ammonia, but no urea. The calculi, which contain uric oxide, have a light brown, or bright brown surface; the fracture is scaly, of a strong lustre, and also of a brown or deep flesh colour; by friction the lustre becomes resinous.

Its formula is $C_5N_2H_2O_2$.

Cystic Oxide.—Discovered by Wollaston; a rare constituent of urinary calculi; an organic base.

Prep.—The calculus is dissolved in aqueous ammonia, and the filtered solution evaporated in the air, when the cystic oxide crystallizes.

Prop.—In the calculus it exists as a yellowish-white confused crystalline mass of a brilliant lustre: crystallizes from its solution in potassa, on the addition of acetic acid, in hexagonal plates; from ammonia, in white transparent scales. It is decomposed by heat, with the evolution of sulphurous and ammoniacal products of an offensive odour. It is readily dissolved by mineral acids, with which it forms crystalline compounds. It forms with hydrochloric acid an anhydrous salt which is composed of 1 eq. of the base and acid. The salt with nitric acid is formed of 1 eq. of acid, 1 eq. of base, and 2 eq. water, the half of which is separated by a temperature of 105°. It is soluble in the pure and carbonated alkalies; but if the solution be heated it is decomposed at first with the evolution of ammonia, but, as the evaporation proceeds, a very combustible gas, which burns with a blue flame, and smells like sulphuret of carbon, is given off. The occurrence of the cystic oxide is so rare, that it is impossible to institute any investigation of this remarkable substance.

According to the analysis of Thaulow, its formula is $C_6NH_6O_4S_2$.

BENZULE.

The term benzule denotes the hypothetical radical of a series of compounds which are produced from the volatile oil of the bitter almond, or are connected with it by certain relations. The oil of bitter almonds itself is always a product of the decomposition of amygdaline, which exists in the kernels of most stone-fruits, and in the leaf of the lauro-cerasus, from which it may be obtained in a variety of ways.

Its formula is $C_{14}H_5O_2$; symb. = Bz; eq. = 106·68.

The compounds of this radical, and the products of their decomposition, are constituted as follow:—

	1 eq. Benzule.	Equiv.	Formulæ.
Benzoic acid, anhydrous . .	106·68+8 Oxygen .	=114·68	BzO.
Benzoic acid, hydrate of . .	106·68+8 Oxygen+9 aq.	=123·68	BzO+aq.
Hyduret of benzule	106·68+1 Hydrogen .	=107·68	BzH.
Chloride do. .	106·68+35·42 Chlorine	=142·10	BzCl.
Bromide do. .	106·68+78·4 Bromine	=185·08	BzBr.
Iodide do. . .	106·68+126·3 Iodine	=232·98	BzI.
Sulphuret do. .	106·68+16·1 Sulphur	=122·78	BzS.
Cyanuret do. .	106·68+26·39 Cyanogen	=133·07	BzCy.
Benzamide . .	106·68+16·15 Amide	=122·83	$BzNH_2$ or BzAd.
Formobenzoic acid	106·68+1 H+1 eq. formic acid	=144·92	$BzH+C_2HO_3$.
Benzoate of hyduret of benzule .	114·68 Benzoic acid + 215·36 Hyd. of Benz.	=330·04	BzO+2BzH.
Hippuric acid .	122·83 Benzam.+49·48 $C_4H_1O_3$+9 aq.?	=181·31	$BzAd+C_4HO_3$+aq.
Hyposulphobenzoic acid . .	85·68 Carb.+4 Hyd.+ 64 Oxy. + 32·2 Sul.+18 aq.	=203·88	$C_{14}H_4O_3S_2O_5$+2 aq.
Brombenzoic acid .	171·36 Carb.+9 Hyd.+ 64 Oxy.+156·8 Brom.+18 aq.	=419·16	$C_{28}H_9O_8Br_2$+2 aq.
Benzole . .	73·44 Carb.+6 Hydrogen	= 79·44	$C_{12}H_6$.
Sulphobenzide . .	85·68 do. + 5 do. + 16·1 Sul.+16 Ox.	=102·78	$C_{14}H_5,SO_2$.
Hyposulphobenzidic acid . .	85·68 Carb.+5 Hyd.+ 32·2 Sul.+40 Ox.	=142·88	$C_{14}H_5,S_2O_5$.
Nitrobenzide .	73·44 Carb.+5 Hyd.+ 14·15 Nit. 32 Ox.	=124·59	$C_{12}H_5NO_4$.
Azobenzide . .	73·44 Carb.+5 Hyd.+ 14·15 Nitrogen	= 92·59	$C_{12}H_5N$.
Chlorobenzole .	73·44 Carb.+6 Hyd.+ 212·52 Chlorine	=291·96	$C_{12}H_6Cl_6$.
Chlorobenzide .	73·44 Carb.+3 Hyd.+ 106·26 Chlorine	=182·70	$C_{12}H_3Cl_3$.
Benzone . .	79·56 Ca.+5 Hy.+8 Ox.	= 92·56	$C_{13}H_5O$.
Hydrobenzamide .	318·24 do. + 18 do. + 14·15 Nitrogen	=350·39	$C_{42}H_{18}N$.
Benzimide . .	171·36 Car.=11 Hyd.+ 14·15 Ni.+32 Ox.	=228·51	$C_{28}H_{11}N_3$.
Benzoine . .	85·68 Ca.+6 H.+16 Ox.	=107·68	$C_{14}H_6O_2$.
Benzile . .	85·68 do.+5 do.+16 Ox.	=106·68	$C_{14}H_5O_2$.
Benzilic acid .	171·36 do.+11 do.+40 Oxy.+9 aq.	=231·36	$C_{28}H_{11}O_5$+aq.
Amygdaline . .	244·80 Car.+27 Hy.+ 14·15 Nit.+176 Oxy.	=455·95	$C_{40}H_{27}NO_{22}$.
Amygdalanic acid .	244·80 Car.+27 Hy.+ 192 Oxy.+9 aq.	=472·80	$C_{40}H_{27}O_{24}$+aq.

BENZOIC ACID.

Benzoic acid exists in gum benzoin, in dragon-blood, &c.; it is formed by the oxidation of the hyduret of benzule in the air, and by the decomposition of many compounds of benzule, and of hippuric acid and amygdaline by oxidizing reagents; by the action of potassa on the essential oils, cinnamon oil, &c. (Mulder.)

Prep.—Gum benzoin, in the form of a coarse powder, either alone or mixed with an equal weight of sand, is spread upon the bottom of a round vessel of cast or plate iron, the sides of which should not be more than three inches high. A sheet of dry bibulous paper is stretched tightly over the opening, and fastened to the sides of the vessel by a little paste. A hat made of thick paper, and of the common form of a man's hat, is made to cover the whole, and tightly tied to the sides of the vessel by a strong string. The vessel is now placed upon sand spread upon an iron plate, below which a fire is kept for 3 — 4 hours. The vapours of the sublimed benzoic acid pass readily through the pores of the bibulous paper, and are deposited in crystals upon the hat; the crystals are prevented from falling back into the iron vessel by the paper which closes its opening. (Mohr.) This is continued as long as a deposite of crystals is observed. Or in the moist way; equal parts of finely powdered gum benzoin and hydrate of lime are most intimately mixed, and then boiled for several hours in 40 parts of water; the filtered liquid must then be evaporated to one-fifth its volume, and treated with hydrochloric acid, when the benzoic acid will crystallize as the solution cools. If less lime be taken, or if a perfect admixture be neglected, the whole will bake into a solid mass in the boiling water; in this case, the hard fragments, after the whole has cooled, must be again mixed with hydrate of lime. Or hippuric acid is boiled for one quarter of an hour in nitric acid of sp. gr. 1·42, after which water is added, and the solution allowed to crystallize. The acid obtained from gum benzoin is purified either by a second sublimation, or being boiled in nitric acid, or by passing chlorine gas through its boiling aqueous solution.

The benzoic acid exists ready formed, and principally in a free state, in the gum benzoin, from which it is separated by sublimation. On boiling hydrate of lime with gum benzoin, the benzoic acid is dissolved, and the resinous parts left; by a strong acid the benzoate of lime is decomposed, and the benzoic acid separated.

Hippuric acid contains benzamide in combination with an organic substance, which is decomposed by the action of the nitric acid; benzamide is decomposed by being boiled with acids into benzoic acid and ammonia.

Prop.—Benzoic acid crystallizes in soft white scales, which are flexible, transparent, and of a mother-of-pearl lustre; or in hexagonal needles. When pure it is inodorous, but if gently warmed it smells like gum benzoin; it has a slightly biting but sweetish taste, produces a burning sensation in the throat, reddens litmus feebly, fuses at 250°, sublimes at 300°, (an appearance of light is frequently observed in the dark,) boils at 462°, yielding a vapour of sp. gr. 4·27; it is not changed by chlorine or by being boiled with dilute nitric acid, but by fuming nitric acid it is converted into a yellow resinous substance of a strongly bitter taste. It is dissolved by concentrated sulphuric acid, but falls upon the addition of water. When heated in open vessels, it emits white odoriferous fumes, which produce a scratching sensation in the throat, are very inflammable, and burn with a smoky flame, without leaving any residue. It is soluble in 200 parts of cold and 25 parts of boiling water; by boiling or evaporating its solution, a portion of the acid volatalizes with the aqueous vapour.

Its formula is $C_{14}H_5O_3 + aq.$, or $BzO + aq.$; eq. $= 123{\cdot}68$.

Benzoate of Ammonia.—Neutral benzoate of ammonia is prepared by dissolving benzoic acid in pure concentrated ammonia, by the aid of heat, till the latter is saturated, when it is allowed to cool. It forms feathery acicular crystals, which deliquesce in a moist air, and are soluble in absolute alcohol.

Its formula is NH_4O, BzO.

The acid salt is formed by boiling and exposing to spontaneous evaporation the neutral salt, when, with the loss of ammonia, it is deposited in large regular crystals.

BENZOIC ACID AND METALLIC OXIDES.

The combination of benzoic acid with the metallic oxides is usually attended with the separation of the water of the hydrate; the soluble benzoates have a strong biting saline taste, and are decomposed by most other acids with the separation of benzoic acid; the same change occurs with the insoluble salts, when the acid which is added forms a soluble salt with the metallic oxide. According to Lecanu and Serbat, many of the benzoates, which are insoluble in water, are taken up by hot solutions of the acetate of potassa and soda, and of nitrate of soda; they are insoluble, on the contrary, in solutions of nitre, and of the sulphate of potassa and soda. The benzoates of the alkalies are decomposed by the destructive distillation into carbonates, and a variety of new products. Exposed to a red heat with an excess of hydrate of lime, the acid is decomposed into benzole and carbonic acid, which unites with the lime. Benzoates of potassa, soda, lithia, and magnesia are very soluble in water, and are with difficulty obtained in crystals.

Benzoates of baryta and strontia are sparingly soluble in cold, but more freely in boiling water, from which they are deposited in fine acicular crystals.

Benzoate of Lime.—Crystallizes with 1 eq. of water of crystallization in brilliant flexible needles or prisms, which require for solution 20 parts of cold, and somewhat less of boiling water. The products obtained by the distillation of this salt have been examined by Peligot. Two fluid products are thus obtained, the benzone $C_{13}H_5O$, and benzole $C_{12}H_6$; then naphthaline $C_{10}H_4$; the residue is carbon and carbonate of lime, and carbonic oxide is evolved. The explanation of the formation of benzone will at once be perceived, when it is mentioned that the anhydrous benzoate of lime contains the elements of benzone and carbonate of lime, or the elements of benzole, naphthaline, carbonic acid, carbonic oxide, and carbon.

$$\begin{array}{llll}
C_{13}H_5O & & & =\text{Benzone.} \\
C \quad O_2 & & & =\text{Carbonic acid.} \\
 & & CaO & =\text{Lime.} \\
\hline
C_{14}H_5O_3 & + & CaO & \text{1 eq. Benzoate of lime.}
\end{array}$$

$$\begin{array}{llll}
C_{10}H_4 & & & =\text{Naphthaline.} \\
C_{12}H_6 & & & =\text{Benzole.} \\
C_2 \quad O_4 & & & =\text{Carbonic acid.} \\
C_2 \quad O_2 & & & =\text{Carbonic oxide.} \\
C_2 & & 2CaO & =\text{Carbon and lime.} \\
\hline
C_{28}H_{10}O_6 & + & 2CaO & =\text{2 eq. Benzoate of lime.}
\end{array}$$

Benzoate of Alumina.—Formed by adding the alkaline benzoates to the salts of alumina, a crystalline precipitate, which is redissolved by heat.

Benzoates of glucina, yttria, and zirconia, are sparingly soluble precipitates.

Benzoates of the protoxides of manganese and iron are soluble salts.

Benzoate of the Peroxide of Iron.—The neutral salt may be obtained in crystals, which are dissolved in water and alcohol with the separation of a basic salt; salts of the peroxide of iron, to the solutions of which so much ammonia has been added, that they lose their acid reaction but are not precipitated, form with the soluble benzoates of the alkalies a reddish-white, or, if an excess of ammonia has been used, a yellowish-brown precipitate, the latter of which is insoluble in water; it falls as a bulky gelatinous mass, which, when dried and exposed to a red heat, leaves 25 per cent. of peroxide of iron. The first-mentioned reddish-white precipitate is decomposed by washing with hot water, when a soluble benzoate of the peroxide of iron is dissolved, and the yellowish-brown basic compound left; the decomposition is prevented by washing with a solution of sal-ammoniac. The benzoate of ammonia is sometimes used with the necessary precautions for separating peroxide of iron from the oxides of manganese, nickel, and zinc, which are not precipitated by it; it cannot be employed if the solution contain alumina, yttria, zirconia, or glucina, as these oxides also form very sparingly soluble salts with benzoic acid.

Its formula is $F_2O_3, 3BzO$.

Benzoate of Oxide of Lead.—A very sparingly soluble white crystalline powder, but soluble in acetic acid, from which it may be obtained in crystals; it contains 2 eq. water, the half of which is retained at 212°. A basic salt is obtained by precipitating a benzoate of the alkalies by the diacetate of lead in the form of a white anhydrous insoluble powder; it is composed of 3 eq. oxide of lead and 2 eq. anhydrous benzoic acid.

Benzoate of Oxide of Silver.—Dilute boiling solutions of a neutral benzoate of an alkali and nitrate of silver being mixed, yield, as they cool, soft flat needles of a white colour and strong lustre, and very similar to benzoic acid, which are anhydrous benzoate of oxide of silver; they blacken by exposure to light. Thrown down from concentrated solutions, it forms a curdy crystalline mass, which, dissolved in hot water, yields a dark-coloured solution owing to the reduction of silver; the salt is again deposited in the described form.

Its formula is $AgOBzO$.

HYDURET OF BENZULE.

Prep.—The essential oil obtained by the distillation of the bitter almond contains benzoic acid, benzoin, and hydrocyanic acid: it is made into a thin paste by being mixed with hydrate of lime, chloride of iron, and water, and redistilled; the oil which passes over is freed from the admixture of water by standing over dry chloride of calcium.

Prop.—A colourless perfectly transparent limpid fluid, of a strong peculiar odour and burning taste; its sp. gr. is 1·043, refracts light strongly, boils at 356°. It is soluble in 30 parts of water, and mixes with alcohol and ether; its vapour is inflammable, and burns with a brilliant but smoky flame; it may be transmitted through red-hot glass tubes without decomposition. By exposure to the air, it absorbs 2 eq. oxygen, and is converted into hydrated benzoic acid; the same change is effected, with the decomposition of water and the evolution of hydrogen, by exposing it to a high temperature with hydrate of potassa. Treated with an alcoholic solution of hydrate of potassa, it congeals in the course of a few moments to a mass of benzoate of potassa, which separates, when the alcohol is found to contain an oily substance not yet examined. By the action of chlorine or bromine, chloride or bromide of benzule, together with hydrochloric or hydrobromic acid is formed; if water be present, there is formed at the same time either benzoate of hyduret of benzule, or benzoic acid. When gently heated with a solution of ammonia, it is converted into hydro-benzamide. It is dissolved by concentrated sulphuric acid with the aid of a gentle heat, but at a higher temperature the solution becomes first red and then black, and evolves sulphurous acid. It unites with anhydrous sulphuric acid, forming a peculiar acid, which is not precipitated by baryta. (Mitscherlich.) Nitric acid dissolves the hyduret of benzule, and converts it with difficulty into benzoic acid. It is poisonous when taken internally in the pure state.

Its formula is $C_{14}H_6O_2$ or $Bz + H$; eq. $= 107{\cdot}68$.

CHLORIDE OF BENZULE.

Discovered by Wöhler and Liebig. It is prepared by passing a stream of chlorine gas through anhydrous hyduret of benzule, as long as hydrochloric acid is evolved; the liquid which has acquired a yellow colour is then heated, to drive off all free chlorine, when it again becomes colourless.

Prop.—A colourless liquid of a peculiar unpleasant odour, which attacks the eyes, and has a sp. gr. = 1·196; the vapour is combustible and burns with a smoky flame tinged with green; it is slowly decomposed into hydrochloric and benzoic acids by cold water, more rapidly by hot water; added to an alkali, a benzoate of the alkali and a metallic chloride are formed; it may be distilled unaltered from anhydrous lime or baryta, and dissolves sulphur and phosphorus without change; when brought into contact with the protochloride of phosphorus, a strong heat is developed, with the formation of the perchloride of phosphorus and a colourless oily substance which has not been further examined. It is decomposed by ammoniacal gas into benzamide and hydrochloric acid; by alcohol, into benzoate of oxide of ethule and hydrochloric acid; it mixes without change with ether, and the bisulphuret of carbon.

Its formula is $C_{14}H_5O_2Cl$, or BzCl.

BROMIDE OF BENZULE.

Discovered by Wöhler and Liebig. Prepared like the chloride. It forms colourless scaly crystals, which become brown by exposure to the air; it is decomposed by water and the alkalies, in the same manner as the chloride; it dissolves without change in ether and alcohol.

Its formula is $C_{14}H_5O_2Br$, or BzBr.

IODIDE OF BENZULE.

Discovered by Wöhler and Liebig. It is prepared by distilling chloride of benzule and iodide of potassium, when it is obtained as a crystalline mass, coloured brown by an excess of iodine. When pure it forms colourless scaly crystals, which are very fusible and become brown in the air; it is acted upon by water and alkalies like the preceding compounds.

Its formula is $C_{14}H_5O_2I$, or BzI.

SULPHURET OF BENZULE.

Discovered by Wöhler and Liebig. Prepared by distilling the chloride of benzule with sulphuret of lead. It forms a yellow oil of a soft crystalline mass, which, when cooled, has a peculiarly unpleasant smell. It is hardly acted on by boiling water, but, when treated with solution of potash, it is slowly converted into benzoic acid and sulphuret of potassium. It is combustible, and dissolves unchanged in alcohol and ether.

Its formula is $C_{14}H_5O_2S$, or BzS.

CYANIDE OF BENZULE.

Discovered by the same chemists. Prepared by distilling chloride of benzule with bicyanide of mercury. A yellow oil, which, when rectified, becomes colourless. Its smell is similar to that of cinnamon, and it irritates the eyes violently. Its taste is pungent and sweetish, with an after-taste of prussic acid. It is inflammable.

Its formula is $C_{14}H_5O_2Cy$, or BzCy.

BENZAMIDE.

Discovered by the same. It is formed when any of the preceding combinations of benzule with supporters of combustion is acted on by dry ammoniacal gas; and it is also a product of the decomposition of hippuric acid by superoxide of lead. Chloride of benzule is saturated with dry ammonia; and the white solid mass produced, which is a mixture of sal-ammoniac and benzamide, is finely powdered, and well washed with cold water to remove the sal-ammoniac. The residue is dissolved in boiling water, and the benzamide crystallizes on cooling. Or hippuric acid is boiled with superoxide of lead, when carbonic acid is disengaged, and hippurate of lead and benzamide are formed, which remain dissolved. Sulphuric acid is now added, cautiously avoiding excess, and the whole is again boiled with a new portion of superoxide of lead. These operations are repeated till all the hippuric acid has been destroyed; and the liquid, when freed from lead, yields crystals of benzamide by evaporation. Chloride of benzule with ammonia produces benzamide and free hydrochloric acid, which is converted into sal-ammoniac by the ammonia in excess; $BzCl + AdH = BzAd + HCl$. Hippuric acid contains the elements of fumaric acid and benzamide (see table). When boiled with superoxide of lead, the organic acid is converted into carbonic acid and water, while the benzamide is liberated.

Benzamide forms right rhombic prisms, or four-sided pearly scales. A concentrated hot solution by slow cooling forms a soft mass of minute crystals, which spontaneously pass into scales of considerable size, after some time. The crystals are colourless and transparent, and melt at about 240°. At a higher temperature they are volatilized, producing an inflammable vapour.

Benzamide is sparingly soluble in cold water; freely and without change in hot water. It is also soluble in alcohol and ether. Alkalies and acids, water being present, decompose benzamide, with the production of benzoic acid and ammonia. When benzamide is gently heated with anhydrous baryta, a violent reaction takes place, with disengagement of heat. Benzoate of baryta is formed; ammonia is disengaged; and a colourless oily liquid distils over, consisting chiefly of benzole.

The formula of benzomide is $Bz + NH_2$, or BzAd.

FORMOBENZOIC ACID; OR FORMIATE OF HYDURET OF BENZULE.

Discovered by Winkler. Prepared by dissolving commercial oil of bitter almonds in water, adding hydrochloric acid, and evaporating in a gentle heat. The dry residue, consisting of formobenzoic acid and sal-ammoniac, is treated with ether, which dissolves the new acid. It is obtained in crystals by the evaporation of the ether, and is decolorized by animal charcoal.

It forms a white granular powder, imperfectly crystallized, or a scaly crystalline mass, which has a strong sour taste, and a faint odour of almonds. When heated, it melts, with disengagement of water, into an oily fluid, which at a higher temperature is decomposed, with a pleasant odour, like that of hawthorn blossom, and leaves behind a bulky coal. It is very soluble in water, alcohol, and ether; and decomposes, with the aid of heat, the salts of acetic, carbonic, and benzoic acids. Its aqueous solution, heated with superoxide of manganese, is resolved into carbonic acid and hyduret of benzule. The same result ensues from the action of nitric acid or of chlorine.

The formobenzoic acid is produced, in the process above described, in the following manner. The commercial oil of bitter almonds contains hydrocyanic acid mixed with the pure oil or hyduret of benzule. In contact with a strong mineral acid and water, the hydrocyanic acid (see that article) is resolved into formic acid and ammonia; the former of which, while nascent, unites with the hyduret of benzule to produce the new acid. Oxidizing agents, by the addition of 2 eq. oxygen, convert the formic acid into carbonic acid and water, while the hyduret of benzule is set free.

The formula of the formobenzoic acid is $C_2HO_3 + C_{14}H_6O_2 + aq.$ or $FoO_3 + BzH + aq.$

FORMOBENZOIC ACID AND METALLIC OXIDES.

Metallic oxides readily combine with this acid, equivalent to equivalent, forming neutral salts. Those with potash and soda are very soluble, and crystallize with difficulty. Formobenzoate of baryta crystallizes in small, hard, transparent prisms. The salt of silver, obtained by mixing solutions of formobenzoate of ammonia and nitrate of silver, appears as a heavy white crystalline and granular precipitate, which is soluble in hot water, and crystallizes on cooling in small anhydrous scales.

BENZOATE OF HYDURET OF BENZULE.

Discovered by Robiquet and Boutron Charlard. It is obtained by saturating common oil of bitter almonds with moist chlorine gas. The liquid, after standing for some time, is converted into a semi-solid mass of crystals, which are to be washed with cold ether. It forms a dazzling white crystalline powder; or short, thin, transparent, and very brilliant four-sided prisms, insoluble in water, soluble in alcohol, slightly soluble in ether. It dissolves easily in alcohol saturated with caustic potash, forming a colourless solution, out of which, after a time, benzoate of potash crystallizes. It melts when heated, and may be sublimed without decomposition. Its formation by the action of moist chlorine on the oil is thus explained: the chlorine converts a part of the oil into hydrated benzoic acid, which, in the nascent state, combines with another portion of the oil. $BzH + 2HO + Cl_2 = BzO,HO + 2HCl$.

Its formula is $C_{14}H_6O_4 + 2(C_{14}H_6O_2)$, or $BzO,HO + 2BzH$.

HIPPURIC ACID.

Discovered by Liebig. Occurs in the urine of the graminivora, such as the horse and cow. It is obtained from the fresh urine by concentrating it in a gentle heat, adding so much hydrochloric acid as to produce an acid reaction, and setting it aside to rest, when impure coloured hippuric acid is deposited in crystals. In the urine it is combined with soda or ammonia, from which combination it is separated by the mineral acid.

When decolorized, which is best effected by animal charcoal, or by chloride of lime with a little muriatic acid, the hippuric acid forms long, transparent or milk-white four-sided prisms, acuminated on two faces; having a slight bitterish taste. It reddens litmus strongly, and melts when heated, concreting into a crystalline mass on cooling. A high temperature decomposes it, when benzoic acid and benzoate of ammonia distil over in red oily drops, which have a strong and agreeable odour of Tonka beans, and soon become solid. The smell belongs to a new oily product. Towards the end of the distillation, hydrocyanic acid is disengaged, and a porous coal is left. Hippuric acid is soluble in 400 parts of cold water, but is easily dissolved at a boiling heat. In oil of vitriol it dissolves without colour by the aid of a gentle heat; in a higher temperature the acid is blackened, benzoic acid sublimes, and sulphurous acid is disengaged. Nitric acid converts it easily into benzoic acid: it dissolves without change in muriatic acid. If gently heated with hyperoxide of manganese and sulphuric acid, it is resolved into carbonic acid, ammonia, and benzoic acid. Boiled with hyperoxide of lead, it yields benzamide and carbonic acid.

If the urine of the horse or cow be left to itself for a long time, or evaporated at a boiling temperature, it yields not a trace of hippuric acid, but only benzoic acid.

The formula of the hippuric acid is $C_{18}NH_8O_5 + aq$. It may be represented as benzamide $C_{14}NH_7O_2$, combined with equisetic or fumaric acid C_4HO_3; or as hyduret of benzule $C_{14}H_6O_2$, combined with hydrocyanic acid C_2NH, and formic acid C_2HO_3. Either of these rational formulæ will explain its ready conversion into benzoic acid.

Rational formula of hippuric acid, $BzAd + C_4HO_3 + aq.$ or $BzH + HCy + FoO_3$.

HIPPURIC ACID AND METALLIC OXIDES.

Hippuric acid forms soluble and crystallizable salts with the alkalies and alkaline earths. Its salts with the oxides of the heavy metals, except that with peroxide of iron, are sparingly soluble in cold, more easily in hot water, and crystallizable. The hippurate of peroxide of iron has the colour and external characters of the benzoate. The hippurate of silver is anhydrous. All the hippurates are decomposed by acids, which separate the hippuric acid: these salts, melted with an excess of hydrate of lime or of potash, give off ammonia and an oily liquid (benzole).

PRODUCTS OF THE DECOMPOSITION OF THE COMPOUNDS OF BENZULE.

HYPOSULPHOBENZOIC ACID.

Synon. Sulphobenzoic Acid. A bibasic acid, discovered by Mitscherlich. It is prepared by adding to a solution of acid hyposulphobenzoate of baryta, diluted sulphuric acid, till the baryta is entirely precipitated. The filtered solution is evaporated, at first over the open fire, and at last in the vacuum of an air-pump with the aid of sulphuric acid, when the hyposulphobenzoic acid crystallizes. In the formation of this acid by the action of anhydrous sulphuric acid on benzoic acid, 2 eq. sulphuric acid and 1 eq. benzoic acid produce water and hyposulphobenzoic acid; $C_{14}H_5O_3 + 2SO_3 = C_{14}H_4O_3 + S_2O_5 + HO$.

Formula, $C_{14}H_4O_3 + S_2O_5 + 2$ aq.

It forms a colourless crystalline mass, deliquescent in a moist atmosphere, having a strong sour taste. It bears a heat of 300° without decomposition; and is not decomposed by boiling with hydrochloric acid nor by nitric acid. Solutions of barytic salts cause in its solution a precipitation of acid hyposulphobenzoate of baryta, in crystals, on cooling, if the solutions be strong.

HYPOSULPHOBENZOIC ACID AND METALLIC OXIDES.

This acid forms two series of salts. The neutral salts contain 2 eq. metallic oxide; the acid salts, dried at 212°, 1 eq. metallic oxide and 1 eq. water. All the salts of this acid, when melted with an excess of hydrate of potash, leave a residue containing a mixture of sulphate, sulphite, and carbonate of potash.

Acid Hyposulphobenzoate of Baryta.—The vapours of anhydrous sulphuric acid are conducted into a dry receiver, containing crystallized benzoic acid, and surrounded with cold water. The sulphuric acid combines with the benzoic acid, forming a translucent mass like turpentine. This mass is mixed with water, as soon as the crystalline structure of the benzoic acid has disappeared. After the acid liquid, by standing, has deposited any excess of benzoic acid, it is neutralized by carbonate of baryta, evaporated and mixed with hydrochloric acid; when on cooling it deposits the acid hyposulphobenzoate of baryta in crystals. It may be rendered perfectly colourless by animal charcoal, and purified from muriatic acid by repeated crystallization. It forms transparent, oblique rhombic prisms, generally twin crystals, soluble in 20 parts of cold water and much less of boiling water. It contains 3 at. water of crystallization, which is expelled by a heat of 212°.

Neutral Hyposulphobenzoate of Baryta is obtained by boiling the preceding salt with carbonate of baryta: it is more soluble than the acid salt; difficultly crystallizable, and bears a heat of 630° without decomposition.

Neutral Hyposulphobenzoate of Lead is obtained by mixing a hot dilute solution of the last salt with one of acetate of lead. It crystallizes on cooling in fine white silky needles arranged in radiated tufts; very sparingly soluble in cold, more easily in hot water. It contains 2 at. water of crystallization.

BROMBENZOIC ACID.

A bibasic acid, discovered by Peligot. To prepare this acid, dry benzoate of silver and bromine, the latter in an open tube, are introduced into a stoppered bottle, which is then closed, and the whole left to itself in the ordinary temperature. The vapour of bromine rising out of the tube is absorbed by the salt, which is decomposed thereby. As soon as the red vapours of unabsorbed bromine are seen in the bottle, the reaction is complete. The mass is now treated with ether, which dissolves brombenzoic acid, and leaves bromide of silver undissolved. By the evaporation of the ether, the acid is obtained in the form of a brown oily matter, which after a time becomes solid and crystalline. It commonly contains a little benzoic acid and an oily matter, to which latter its colour is owing. To purify it, it is combined with potash, the solution decolorized by animal charcoal, and the salt then decomposed by nitric acid, when pure brombenzoic acid separates. In this process, when bromine acts on benzoate of silver, both the benzoic acid and the oxide of silver are decomposed. From 2 at. oxide of silver, 2 at. oxygen pass over to the elements of the acid. Bromide of silver is formed, 1 eq. hydrogen out of 2 at. benzoic acid unites with 1 eq. bromine; and is separated as hydrobromic acid. Finally 1 eq. bromine takes the place of the hydrogen. ($C_{28}H_{10}O_8 + Ag_2$) $+ Br_4 = (C_{28}H_9BrO_8) + 2AgBr + HBr$.) The anhydrous brombenzoic acid which is here formed, combines with 2 at. water when separated from its salts by a stronger acid.

Its formula is $C_{28}H_9BrO_8 + 2$ aq.

It forms a colourless crystalline mass, fusible at 212°, subliming at 480°, with a partial decomposition, and leaving a residue of carbon. It is sparingly soluble in water, very soluble in alcohol, ether, and pyroxylic spirit. It is inflammable, and burns with a smoky flame edged with green. Its solutions, added to nitrate of silver, produce no precipitate of bromide of silver.

BROMBENZOIC ACID AND METALLIC OXIDES.

Brombenzoic acid forms soluble salts, some of which crystallize, with the alkalies, alkaline earths, and the oxides of zinc, cobalt, nickel, mercury, and silver; and sparingly soluble salts with oxides of lead and copper and protoxide of mercury. The brombenzoate of peroxide of iron is insoluble, and resembles the benzoate of that oxide.

BENZOLE (BENZINE).

First discovered by Faraday among the products of the destructive distillation of organic substances; afterwards noticed by Mitscherlich as the chief product of the decomposition of crystallized benzoic acid by hydrate of lime at a high temperature.

To prepare it, 1 part of crystallized benzoic acid, intimately mixed with 3 parts of slaked lime, is subjected to distillation. The oily liquid obtained is purified by re-distillation with water, or with hydrate of lime and dry lime.

It is a clear colourless liquid of a peculiar, ethereal, agreeable odour; boils at 186°; its sp. g. in the liquid form is 0·85; in the form of vapour 2·738 at 60°. It freezes at 32° into a crystalline mass resembling loaf-sugar, which melts again at 44°. It is insoluble in water, soluble in ether and alcohol, not altered by hydrated acids, not acted on by potassium, which retains its lustre in the liquid. From its sp. g. in the state of vapour, it appears to contain 3 vol. hydrogen and 3 vol. carbon vapour. Its formula is C_2H. But it is probable that the formula $C_{12}H_6$ represents its true atomic weight. It is polymeric with formule, a hypothetical radical hereafter to be described.

Its production from benzoic acid is thus easily explained; for if from 1 at. crystallized benzoic acid we take away (by the lime) 2 at. carbonic acid, benzole remains. $C_{14}H_6O_4—C_2O_4=C_{12}H_6=6C_2H$.

PRODUCTS OF THE DECOMPOSITION OF BENZOLE.

Sulphobenzide.—Discovered by Mitscherlich. Benzole and anhydrous sulphuric acid are brought together, when they form a viscid liquid, without special signs of decomposition. The compound dissolves in a small quantity of water, but by the addition of more water sulphobenzide is precipitated, which may be obtained in crystals by solution in ether and spontaneous evaporation. Here 1 at. sulphuric acid and 1 at. benzole produce 1 at. water and 1 sulphobenzide.

It is a colourless, inodorous, indifferent body, melts at 212°, and sublimes without decomposition at a higher temperature.

Its formula is $C_{12}H_5SO_2$.

Hyposulphobenzidic Acid.—This acid is contained in the liquid from which, in the above process, the sulphobenzide has separated. It is also formed by dissolving sulphobenzide in oil of vitriol, and by the action of the fuming sulphuric acid on benzole. It may be considered as composed of oil of vitriol and sulphobenzide, which explains its formation. It is obtained pure by decomposing the hyposulphobenzidate of copper by sulphuretted hydrogen. It forms a very sour liquid, which crystallizes when evaporated to the consistence of syrup, and bears a heat of nearly 400° without decomposition.

Its formula is $C_{12}H_5S_2O_5$ in its salts.

Hyposulphobenzidate of Baryta.—A soluble salt, crystallizing indistinctly. It is obtained by dissolving in fuming oil of vitriol as much benzole as it will take up, mixing the solution with water, filtering to separate the sulphobenzide, and neutralizing the liquid with carbonate of baryta. A second filtration separates the sulphate of baryta which is formed at the same time, and the filtered liquid contains the barytic salt in question.

Hyposulphobenzidate of Copper.—The solution of the preceding salt is accurately precipitated by sulphate of copper, and the sulphate of baryta separated by filtration. The filtered liquid, being evaporated, yields on cooling large regular crystals of hyposulphobenzidate of copper. This salt contains water of crystallization, which it loses at 340°. It may be heated to 430° without decomposition.

NITROBENZIDE.

Discovered by Mitscherlich. Prepared by adding to warm, red, and fuming nitric acid as much benzole as it can dissolve, adding water, and allowing the whole to cool. Nitrobenzide precipitates. It is at 60° a yellow liquid of an intensely sweet taste, and an odour like that of cinnamon. It boils at 415°; sp. g. of the liquid 1·209, of the vapour 4·294. It crystallizes at 38° in needles, insoluble in water, soluble in alcohol and ether. Nitrobenzide is soluble in diluted acids, from which it is precipitated by water. It is decomposed by oil of vitriol, but not by alkalies.

Its formula is $C_{12}H_5NO_4$.

AZOBENZIDE.

Discovered by Mitscherlich. Nitrobenzide is dissolved in alcohol, and heated with solid hydrate of potash: the red solution which is formed is then distilled. At first alcohol, then azobenzide distils over, and they are collected separately. It forms large red crystals, fusible at 150°, boiling at 380°.

Its formula is $C_{12}H_5N$. Its production as yet is unexplained.

CHLORIDE OF BENZOLE.

Discovered by Mitscherlich and Peligot. It is formed by the action of chlorine gas on benzole aided by the sun's rays. The benzole changes into a crystalline mass of chloride of benzole, which is a colourless solid, fusible at 270°, and boiling with partial decomposition at 550°. It is insoluble in water, soluble in alcohol and ether, and crystallizes easily from the latter solution.

Its formula is C_2HCl, or $C_{12}H_6Cl_6$.

CHLOROBENZIDE.

Discovered by Mitscherlich. When the preceding substance is distilled, half of its chlorine and hydrogen are separated, especially with the aid of an alkali, such as hydrate of lime. It forms a colourless oily liquid, which boils at about 410°. Sp. g. of the liquid at 45°, 1·457; of the vapour, 6·37.

Its formula is $C_{12}H_3Cl_3$.

Benzole forms corresponding compounds with bromine.

BENZONE.

Discovered by Mitscherlich and Peligot. Syn. Carbobenzide of Mitscherlich. It is produced in the distillation of benzoate of lime. (See that salt.) To obtain it, the raw product of the distillation of benzoate of lime is heated, first in the water-bath, and then gradually up to 920°, as long as benzole passes over. The residue is then distilled separately. The product is now benzone, holding in solution a certain quantity of naphthaline, which, by exposure to a cold of —5°, crystallizes out, and leaves, according to Peligot, pure benzone. Benzone is a colourless or pale-yellow, viscid, oily liquid, heavier than water. It is decomposed by sulphuric acid or chlorine, but not by nitric acid or caustic potash.

Its formula is $C_{13}H_5O$. It may be derived from benzole and carbonic acid, by the removal of the elements of water; $C_{12}H_6 + CO_2 = (C_{12}H_5 + CO) + HO$.

PRODUCTS OF THE DECOMPOSITION OF HYDURET OF BENZULE.

HYDROBENZAMIDE.

Discovered by Laurent. To prepare it, pure hyduret of benzule is mixed in a stoppered bottle with twenty times its volume of concentrated aqua ammoniæ, and the mixture is kept for some hours at a temperature of from 100° to 120°. A crystalline mass is formed, which is washed with cold ether, and pure hydrobenzamide is left, which may be obtained in large and regular crystals by solution in alcohol and spontaneous evaporation. It forms regular octahedrous or rhombic prisms, tasteless, inodorous, and colourless; melting at 230°, and burning with a smoky flame. When distilled, it is decomposed with a residue of carbon: it is insoluble in water, soluble in alcohol, sparingly soluble in ether. The alcoholic solution, by boiling, is resolved into ammonia and hyduret of benzule. When heated with hydrochloric acid, it is quickly and easily resolved into hyduret of benzule and sal-ammoniac. Hydrate of potash hardly acts on it; but it undergoes a spontaneous decomposition by keeping. It is produced by the action of 2 eq. ammonia on 3 at. of hyduret of benzule, forming 1 at. hydrobenzamide, and 6 at. water. $3(C_{14}H_6O_2 + {}_2(NH_3) = 6HO + (C_{42}H_{18}N_2)$; which last is the formula of hydrobenzamide.

When the raw oil of bitter almonds is employed instead of the pure in this process, a yellow resinous mass is obtained, which is a mixture of hydrobenzamide, benzhydramide, azobenzule, and nitrobenzule. (Laurent, Ann. de Ch. et de Ph. t. lxvi. p. 180.)

Benzhydramide has the same composition as hydrobenzamide. When the above-mentioned resinous mass is boiled with ether, both these substances are dissolved. By continued boiling, the hydrobenzamide is resolved into ammonia and hyduret of benzule. The benzhydramide crystallizes on cooling, mixed with azobenzule. Boiling alcohol dissolves the former, leaving the latter undissolved; and the benzhydramide is purified by repeated crystallization out of alcohol. It crystallizes in rectangular or six-sided prisms, melts when heated into a transparent liquid, which when cold is not crystalline. A stronger heat decomposes it. It is not altered by boiling hydrochloric acid. The crystals are commonly mixed with others, whose form and reactions seem to indicate that they are a different substance.

Azobenzule.—The residue of the preparation of benzhydramide contains azobenzule and nitrobenzule. This residue is boiled with 100 parts of alcohol, which on cooling deposits crystals of azobenzule. It forms a fine white crystalline powder, decomposable by heat.

Its formula is $C_{42}H_{15}N_2$: according to which it may be formed by the action of 3 at. benzule and 2 eq. ammonia. $3(C_{14}H_5O_2) + 2NH_3 = 6HO + C_{42}H_{15}N_2$.

Nitrobenzule.—The insoluble residue of the preparation of the last substance is nitrobenzule. It forms a white tasteless powder, nearly insoluble in alcohol. By alkalies it is converted into another crystalline body not examined.

BENZIMIDE.

Discovered by Laurent. An ingredient of the raw oil of bitter almonds, from which it separates under certain circumstances. It forms white, inodorous, pearly needles and lamellæ, very light and flocky; insoluble in water, very sparingly soluble in alcohol and ether, rather more so in pyroxylic spirit. It melts at about 300°; is inflammable, burns with a red, smoky flame; and is dissolved and decomposed by nitric, hydrochloric, and sulphuric acids; the latter of which is coloured by it dark indigo-blue, or green if moisture be present. According to Laurent, it is resolved by acids into ammonia and benzoic acid; but, for want of material, his experiments are not to be considered decisive.

Its formula is $C_{28}H_{11}O_4N$. Nothing is known of the way in which it is formed; but if the formula be correct, it may be considered as anhydrous benzoate of ammonia, *minus* 2 at. of water.

COMPOUNDS ISOMERIC WITH BENZULE.

BENZOINE.

Discovered by Robiquet and Boutron Charlard. It is produced by the contact of alkalies with the commercial oil of bitter almonds; but not with the pure hyduret of benzule. When the raw oil is distilled with hydrate of lime and protochloride of iron, the residue is a mixture of benzoine with lime and hydrated protoxide of iron. It is treated with hydrochloric acid, which dissolves the iron and lime; and the undissolved benzoine is purified by solution in alcohol with the aid of animal charcoal. Or the raw oil is dissolved with the aid of heat in lime or baryta water, and the solution, in a stoppered bottle, is kept for several hours at the temperature of 212°, when it becomes filled with fine, snow-white, flaky crystals, which, if dissolved in hot alcohol, are deposited in a state of purity on cooling. The best method of preparing it consists in mixing a solution of caustic potash in alcohol, with its equal volume of raw oil of bitter almonds. After a little time the mixed liquids become apparently solid from the quantity of small crystals of benzoine formed in them; these must be purified by crystallization from alcohol. They form transparent, colourless, very brilliant prisms, without smell or taste; melting at about 230°, volatilizing unchanged at a higher temperature; inflammable, burning with smoke; insoluble in cold, little soluble in hot water, more soluble in boiling than in cold alcohol. Benzoine is soluble in oil of vitriol with a violet-blue colour; if the solution be heated, becoming brown, green, and at last black, with disengagement of sulphurous acid. It is insoluble in aqueous solutions of the alkalies. If melted with hydrate of potash, benzoate of ammonia is formed, with disengagement of hydrogen gas. An alcoholic solution of potash dissolves it with a violet-blue colour; and if the solution be boiled, it passes into benzilic acid. Its vapour, passed through a red-hot glass tube, is converted into an oily substance with the odour of bitter almonds (hyduret of benzule). It is decomposed by bromine. Chlorine gas, when made to act on melted benzoïne, deprives it of some hydrogen, and converts it into benzile.

The part which hydrocyanic acid plays in the production of benzoine by the action of alkalies on hyduret of benzule is still obscure. It is certain that benzoine cannot be obtained from pure hyduret of benzule; but that it appears after a few hours, when a little hydrocyanic acid is added to a hot solution of the pure hyduret in barytic water, if the solution be kept hot. After the separation of the benzoine, the liquid contains ammonia and benzoic acid, with a mere trace of formobenzoic acid.

Formula of benzoine, $C_{14}H_6O_2$. It is therefore isomeric with hyduret of benzule.

Hydrobenzoinamide, or *Benzoinamide*, has the same composition as hydrobenzamide. It is obtained by gently heating benzoine with aqua ammoniæ; and forms a white, tasteless, inodorous powder, volatile without decomposition.

HYDROCYANATE OF BENZOINE.

Discovered by Zinin.—To procure this compound, a mixture of 4 parts of oil of bitter almonds, and 1 part of anhydrous prussic acid is added to 1 part of a solution of caustic potash of sp. g. 1·25, diluted with 6 times its bulk of alcohol. The whole should be gently heated, and laid aside for twenty-four hours, after which, fine white flocculent crystals form, which may be purified by crystallization from alcohol. It is difficultly soluble in alcohol and ether; in sulphuric acid it dissolves with a green colour; in muriatic acid, potash-ley, and water, it is insoluble. Its formula is

$C_{46}H_{18}N_2O_4$; hence it is formed of 3 atoms of hyduret of benzule, and 2 atoms of prussic acid, minus 2 atoms of water.

BENZILE.

Syn. Benzule of Laurent, who first obtained it. To prepare it, chlorine gas is passed over melted benzoine as long as hydrochloric acid escapes. The crystalline mass which remains after cooling is dissolved in hot alcohol, which on cooling deposits crystals of pure benzile. It is sometimes found along with benzoine in the residue of the distillation of raw oil of bitter almonds with hydrate of lime and protochloride of iron; and may easily be separated from that substance by crystallization. But the most simple method of procuring it is, to add 2 parts of pure nitric acid to 1 part of benzoine, and to expose this mixture to a gentle heat; violent action ensues from the escape of nitrous acid, and the benzile appears as a colourless oil on the surface of the liquid. (Zinin.)

Benzile forms large sulphur-yellow, translucent, regular six-sided prisms, belonging to the rhomboidal system; tasteless, inodorous; melting about 200°; insoluble in water, soluble in alcohol and ether; of the hardness of sugar, crackling between the teeth; volatile without decomposition; inflammable, burning with a red smoky flame; soluble in oil of vitriol, from which it is precipitated by water; insoluble in an aqueous solution of potash, with which it may be boiled without decomposition; but soluble with decomposition in an alcoholic solution of potash, to which it gives a violet-blue colour, while it passes into benzilic acid.

Formula of benzile, $C_{14}H_5O_2$. It has therefore the composition of the hypothetical radical benzule.

HYDROCYANATE OF BENZILE.

Discovered by Zinin.—When a hot solution of benzile in alcohol is mixed with an equal bulk of anhydrous prussic acid, large rhombic colourless crystals of this substance are formed. They are insoluble in water and muriatic acid, and decomposed by ammonia and nitric acid into benzile and prussic acid. Its formula is $C_{14}H_5O_2 + CyH = C_{16}H_6NO_2$; hence it consists of 1 atom of benzile, and 1 atom of prussic acid.

BENZILIC ACID.

Discovered by Liebig. Obtained by boiling benzoine or benzile, with a concentrated alcoholic solution of potash, in which it dissolves easily with a violet-blue colour, which disappears by continued boiling. The alkaline solution is added as long as it causes any blue colour after the previous portion has been decolorized by boiling, and the solution is then carefully neutralized by hydrochloric acid, by which means a resinous matter is separated. To the filtered solution is added an excess of hydrochloric acid, and on cooling the benzilic acid crystallizes.

Benzilic acid forms colourless, transparent, brilliant, rhombic crystals, soluble in cold water sparingly, in hot more easily; fusible at 230°, not volatile. When strongly heated, it yields benzoic acid which sublimes, a violet-coloured vapour, and a residue of carbon. If brought in contact with cold oil of vitriol, a lively carmine-red colour is developed.

If to the elements of 2 at. benzile those of 2 at. water be added, we have the composition of benzilic acid; in which, however, one atom of water is basic, as it can be replaced by metallic oxides.

Its formula, therefore, is $C_{28}H_{11}O_5 + aq$.

The quantity of the resinous matter above-mentioned formed with it is always trifling, and most probably is not essentially connected with it. The oxygen of the atmosphere seems to have some share in the production of benzilic acid from benzoine; but these reactions have not yet been sufficiently investigated.

Of the salts of benzilic acid, the potash salt and silver salt have been examined; the potash salt crystallizes in large transparent tables, the silver salt is $C_{28}H_{11}O_5, AgO$, and forms a white crystalline powder insoluble in water.

Azobenzoide.—Oil of bitter almonds, prepared by distillation per descensum with steam, gave, when put in contact with ammonia, a brown viscid mass, which, when deprived by means of alcohol and ether of everything soluble in those menstrua, left a residue of azobenzoide, in the form of a white powder, decomposable by heat.

Formula, $C_{42}H_{16\frac{1}{2}}N_{2\frac{1}{2}}$? (Laurent.)

COMPOUNDS BELONGING TO THE SERIES OF BENZULE.

AMYGDALINE.

Discovered by Robiquet and Boutron Charlard. An ingredient of bitter almonds and of the berries (and leaves?) of the cherry-laurel (Prunus Laurocerasus, *Winkler*). In order to obtain it, bitter almonds are finely powdered, and strongly pressed between warm iron plates to remove the fixed oil. The residue is repeatedly boiled with alcohol of 93 — 94 per cent. The decoctions are united, distilled in the water-bath till the alcohol is driven off, and the syrupy liquid which is left is diluted with water, a little ferment is added, and the whole is left to itself in a warm situation. Fermentation soon commences, and, after it has ceased, the liquid is filtered, evaporated in the water-bath to the consistence of syrup, and mixed with alcohol of 94 per cent. The amygdaline is almost entirely precipitated in the form of a white crystalline powder. This is squeezed out, and purified by new solutions and crystallizations in alcohol. Amygdaline exists ready formed in the bitter almonds, and is dissolved by the alcohol along with sugar. The latter substance impedes the crystallization of the amygdaline; and this impediment is removed by the fermentation. About 3 or 4 per cent. of amygdaline are obtained.

Amygdaline crystallizes out of alcohol in silky scales, or short needles, which have no smell, but a faint taste of bitter almonds. At a high temperature it is decomposed with an odour of hawthorn blossom, and leaves a voluminous coal. It is hardly soluble in cold alcohol, but somewhat soluble at the boiling temperature. The crystals contain alcohol, which they lose on exposure to the air. It is very soluble in water. A solution saturated at 104° gives on cooling large silky transparent prisms, containing 6 at. (10·57 per cent.) of water; of which they lose, when placed under a jar near oil of vitriol, 2 at. (3·52 per cent.) In dry chlorine it undergoes no change: in moist chlorine it is decomposed, swelling up, and leaving a white powder, soluble in water and in alcohol, not yet examined. When acted on by dilute nitric acid, or by hyperoxide of manganese and sulphuric acid, it is resolved into ammonia, hyduret of benzule, benzoic acid, formic acid, and carbonic acid, the latter passing away as vapour and gas during the distillation. With caustic alkalies it is resolved into amygdalinic acid and ammonia; with hypermanganate of potash it is resolved into cyanate and benzoate of potash.

Formula, $C_{40}H_{27}O_{11}N$.

AMYGDALINIC ACID.

Discovered by Wöhler and Liebig. Obtained by dissolving amygdaline in barytic water, and boiling the solution as long as ammonia is evolved. The baryta is then precipitated by sulphuric acid, and the filtered liquid evaporated in the water-bath. It forms a colourless transparent, amorphous mass, having a pleasant acid taste, which deliquesces in moist air, and is insoluble in alcohol and ether. When heated with nitric acid, or with hyperoxide of manganese and sulphuric acid, it produces hyduret of benzule, with formic and carbonic acids. It forms with all bases salts soluble in water, and with oxide of lead a basic salt which is insoluble. These salts are little known. The formula of amygdalinic acid is $C_{40}H_{26}O_{12} + aq$. In the anhydrous amygdalate of baryta, the atom of basic water in the above formula is replaced by an atom of baryta.

APPENDIX TO THE COMPOUNDS OF BENZULE.

Aqueous solution of hyduret of benzule, containing also hydrocyanic acid, or distilled water of bitter almonds.

Prep.—Two pounds of powdered bitter almonds, freed from all fixed oil by pressure between heated iron plates, are made with cold water into a thin paste in a stoppered vessel. After macerating for twelve hours it is distilled; and in order to avoid burning the mass, this is best done by means of steam, or in a bath of chloride of calcium. Two pounds of liquid are distilled off.

It is a somewhat milky liquid, having a strong smell and taste both of hydrocyanic acid and of oil of bitter almonds. It generally deposits, when allowed to rest, a certain quantity of oil (hyduret of benzule, containing hydrocyanic acid). After 24 hours the water becomes clear; and frequently becomes again turbid in bottles containing air. Freshly prepared, it contains in 1 ounce $1\frac{1}{14}$ grain of anhydrous hydrocyanic acid (equal to about 33 drops of the ordinary medicinal acid of this country, containing 3·2 per cent. of anhydrous acid), but its strength in this respect diminishes very much by long keeping. This water possesses this peculiarity, that the hydrocyanic acid contained in it cannot be at once precipitated as cyanide of silver by the addition of nitrate of silver. This precipitation takes place, however, perfectly, if nitrate of silver and ammonia be both added to the water, and the ammonia neutralized after a time by nitric acid, when the cyanide of silver separates. A solution of pure hyduret of benzule, to which hydrocyanic acid has been added, acts exactly in the same way. The distilled water of bitter almonds, mixed with hydrochloric acid, and evaporated, yields a residue of formobenzoic acid and sal-ammoniac. It is used in medicine, and is poisonous.

LAUREL WATER.

Two parts of the fresh leaves of prunus laurocerasus, L. are distilled with water till 3 parts have passed over. This water resembles the preceding, and is used for the same purposes.

Most pharmacopœias recommend an addition of spirit of wine to these distilled waters. Before the distillation this is useless, and even hurtful. Afterwards it prevents turbidity, but gives the water a tendency to become acid.

ON THE FORMATION OF HYDURET OF BENZULE FROM BITTER ALMONDS.

The white part both of sweet and bitter almonds consists chiefly of a substance which is very remarkable on account of a peculiar decomposition which it suffers in contact with amygdaline and water, and produces also in the amygdaline. Wöhler and Liebig named this substance Emulsine. Robiquet has obtained it in a separate form, and calls it Synaptase. It is soluble in water, and is precipitated by alcohol in white flocks, which may be again dissolved in water. It is precipitated neither by acids nor by acetate of lead. At 140° it coagulates like albumen; it contains nitrogen, and when boiled with alkalies is resolved into ammonia and a new acid. If 10 parts of amygdaline be dissolved in 100 of water, and mixed with an emulsion of sweet almonds, or with a solution of 1 part of synaptase in 10 of water, the reaction above alluded to instantly commences; the liquid, without losing its transparency, becomes slightly opalescent by reflected light; the smell of bitter almonds is perceived in the solution; and when distilled, both hydrocyanic acid and hyduret of benzule pass over with the vapour of water. The residue in the retort is turbid from coagulated synaptase; and if evaporated yields a very sweet syrup, which contains crystallizable sugar, and a fixed acid, which is perceived after the sugar has been destroyed by fermentation. The quantity of sugar is greater than could be formed out of the elements of the quantity of amygdaline originally present, so that the elements of the synaptase appear to be essentially concerned in its production.

The complete decomposition depends on the quantity of the water in which the amygdaline and synaptase are dissolved; if there be less than is required to dissolve the hyduret of benzule produced, a proportionate quantity of amygdaline remains undecomposed. Coagulated synaptase has no appreciable action on amygdaline.

These facts serve to explain a series of phenomena which have long been known. In bitter almonds amygdaline and synaptase, along with fixed oil, are present, but in such a form that the two former cannot act on each other. The drying of the almonds, by removing all water, also prevents this reaction. By squeezing the bruised almonds, the fixed oil is separated; and the marc, if boiled with alcohol, yields to that solvent the amygdaline, while the synaptase is coagulated.

When the marc is moistened with cold water, the reaction above described instantly commences. The smell and taste of hydrocyanic acid and hyduret of benzule are perceived. If the emulsion be made with little water, a corresponding quantity of amygdaline remains undecomposed, and may be obtained in crystals by means of alcohol. But if there be a sufficient quantity of water, all traces of amygdaline disappear after a time.

If the newly pressed marc be thrown into boiling water, the synaptase is brought by the heat into that state in which it ceases to act on the amygdaline; and if the marc be now distilled with water, neither hydrocyanic acid nor hyduret of benzule is formed at all.

When we wish, therefore, to obtain the oil, or the distilled water, for medical use, we must, for the above reasons, make the pressed marc into a paste with about 20 parts of lukewarm water, and leave the mixture to itself for 24 hours.

One hundred parts of amygdaline yield 47 of raw oil, containing 5·9 of anhydrous hydrocyanic acid. Hence 17 grains of amygdaline, dissolved in a fluid ounce of an emulsion of sweet almonds, yield a liquid containing one grain of anhydrous acid, which does not require to be distilled. This mixture has been proposed as a uniform preparation, to replace the very variable distilled water, by Wöhler and Liebig. The great tendency both of hydrocyanic acid and hyduret of benzule to be changed when in contact with air and water into many new compounds, is the cause of the loss of strength which the distilled water undergoes when long kept. But amygdaline keeps perfectly in the solid form; and when the above mixture is made only in small quantities, as it is prescribed, it will be found perfectly uniform in strength, as it need not be kept long.

The leaves of the cherry-laurel seem in like manner to contain amygdaline, along with some substance which, like synaptase, has the power of decomposing it; for the laurel water contains the same ingredients as the distilled water of bitter almonds.

Amygdaline contains in 1 atom the elements of 1 eq. hydrocyanic acid, 2 eq. hyduret of benzule, 1 at. sugar ($C_6H_5O_5$), 2 eq. formic acid, and 7 at. water. Amygdalinic acid contains the elements of 2 eq. hyduret of benzule, 1 of sugar, 3 eq. of formic acid, and 6 of water. Robiquet (Journ. de Pharm. 1838, p. 328) has made known a process by which we may obtain synaptase, the peculiar substance above-mentioned, which possesses the property of decomposing amygdaline in contact with water. It is as follows: —Sweet almonds, freed by pressure as completely as possible from fixed oil, are mixed with twice their weight of water, and, after macerating for two hours, exposed to pressure in a cloth. The squeezed liquid is filtered, and acetic acid added as long as it causes a thick white precipitate of vegetable albumen. Acetate of lead is then added to separate gum; and a liquid is thus obtained, which contains only free acetic acid, acetate of lead, sugar, and synaptase. The oxide of lead is removed by sulphuretted hydrogen, and the synaptase is then thrown down by the addition of alcohol. The sugar and free acetic acid remain dissolved. The precipitate is washed with alcohol, and dried in vacuo over sulphuric acid.

When dry, it forms a yellowish-white, hard, brittle, opaque, horny mass, very soluble in cold water. The solution speedily undergoes spontaneous decomposition, becomes muddy, and acquires a putrid odour. Tincture of iodine produces in the fresh solution an intense rose-red colour, without causing a precipitate. The composition of synaptase is not yet ascertained.

When an emulsion of sweet almonds is deprived of all fixed oil by means of ether, a clear viscid liquor is obtained, which, when mixed with alcohol, gives a thick white precipitate, drying into a semi-transparent horny mass. This is the substance which was called emulsine by Wöhler and Liebig; but which, as would appear from Robiquet's process above described, contains vegetable albumen mixed with synaptase. Richardson and Thomson jun. have analysed this emulsine, but their results need not be quoted here, as the substance is admitted to have been a mixture. They found that when boiled with baryta, or caustic alkalies, it yielded abundance of ammonia.

THEORETICAL VIEWS ON THE CONNECTION OF THE COMPOUNDS OF BENZULE.

In the foregoing pages the compounds of benzule have been described according to a theory which naturally connects itself with the history of the simple radicals; but with such variations as arise from the complex nature of the supposed radical benzule, and which were to be looked for beforehand. But the oil of bitter almonds may also be viewed as a compound of 2 at. benzoic acid with a carbo-hydrogen, represented by the formula $C_{14}H_5 + 3H$. The true radical of the benzoic compounds would thus be the carbo-hydrogen $C_{14}H_5$. Benzoic acid would be the highest degree of oxidation of this radical, $C_{14}H_5O_3$; and the oil of bitter almonds would contain the corresponding compound of hydrogen, $C_{14}H_5,H_3$, combined with two atoms of benzoic acid. $C_{14}H_5H_3 + 2\,(C_{14}H_5O_3) = C_{42}H_{18}O_6 = 3\,(C_{14}H_6O_2)$. The chloride of benzule on this view would be a compound of 2 at. benzoic acid and 1 of the corresponding chloride of this new radical, $C_{14}H_5Cl_3 + 2C_{14}H_5O_3 = 3\,(C_{14}H_5O_2Cl)$. In the mineral or inorganic kingdom we have analogous compounds, as in the chlorochromic acid, molybdate of chloride of molybdenum, &c. On this view, first suggested by Dumas, it is difficult to explain the formation of hydrobenzamide, benzamide, and other compounds. Mitscherlich, again, considers the sublimed benzoic acid as anhydrous, and composed of 1 at. benzole $C_{12}H_6$, and 2 at. carbonic acid C_2O_4. When brought in contact with a base, according to him, 1 at. hydrogen from the benzole, and 1 at. oxygen from the carbonic acid, would combine to form water; and an anhydrous benzoate would contain benzide $C_{12}H_5$, and anhydrous oxalic acid C_2O_3. There is no evidence sufficient to determine which of these three different views is actually correct.

SALICULE.

Under the name of hyduret of salicule, a peculiar acid was made known by Piria, who discovered it as a product of the decomposition of salicine. The interest excited by its uncommon properties was increased in an unwonted degree by some researches of Dumas, which rendered it very probable that this substance was identical with one of the ingredients of an essential oil, first obtained by Pagenstecher by distilling the flowers of spiræa ulmaria (meadowsweet), and described by Löwig as hyduret of spiroyle. Ettling, by very exact analyses, put beyond all doubt the identity of these two substances. According to Ettling and Piria, the composition, both of the oil produced by the decomposition of salicine, and of the oil of spiræa ulmaria, is the same as that of crystallized benzoic acid. This oil, which is an acid, combines with bases to form salts which have the same composition as the benzoates; but the difference in their properties is so great that they cannot be confounded together. From the reactions of this acid with chlorine and with caustic alkalies, Dumas drew the conclusion, that it contains a radical, which may be regarded as a higher degree of oxidation of benzule. With hydrogen this radical forms hyduret of salicule; with oxygen, saliculic acid. In contact with chlorine, bromine, and iodine, the hydrogen of the hyduret is replaced by an equivalent of these elementary bodies; a reaction which he compares to the formation of chloride of benzule from the hyduret of benzule. The following formulæ represent these views:—

$C_{14}H_5O_2$	Benzule.	$C_{14}H_5O_4+H$	Hyduret of salicule.
$C_{14}H_5O_3$	Benzoic acid.	$C_{14}H_5O_4+O$	Saliculic acid.
$C_{14}H_5O_4$	Salicule.	$C_{14}H_5O_4+Cl$	Chloride of salicule.
$C_{14}H_5O_5$	Saliculic acid.	$C_{14}H_5O_4+Br$	Bromide of salicule.

If we merely look at the composition of these compounds, this view of them appears extremely probable. Indeed it was originally proposed by Löwig for the oil of spiræa, some years before it was possible to suspect the identity of two substances obtained from sources so different; although his analytical results, in regard to the actual composition of that body, were not confirmed by subsequent researches. The late investigations into the constitution of many salts of organic acids have shown that many, perhaps all, of these acids must be regarded as hydrogen acids; but while for this reason we prefer the view of Dumas, above given, we yet think it better, till these important questions are finally decided, to retain, in the description of these bodies, the method usually followed in inorganic chemistry for acids containing oxygen.

According to the usual method then, the formula of the hyduret of salicule, or hydrosaliculic acid, will be $C_{14}H_5O_3 + HO$; and it will thus be isomeric with benzoic acid. It may, on this view, be called the *hydrated saliculous acid.* This acid possesses two distinct characters, in its relations to other bodies: towards bases it acts as a powerful acid; towards ammonia and salt radicals it conducts itself exactly as hyduret of benzule.

Now it would appear from the action of ammonia on this acid, and on the chloride of salicule, and from the fact that this acid can form acid salts with potash and soda, that the saliculous acid stands to benzoic acid in the same relation as fulminic or cyanuric acids to cyanic acid; in such wise, that, considered as a hydrogen acid, the saliculous acid contains twice the radical of benzoic acid with 2 atoms, or thrice that radical with 3 atoms of hydrogen. Considered as oxygen acids, the benzoic acid would be a monobasic, the saliculous acid a bibasic or a tribasic acid.

The compounds formed by the action of chlorine or bromine on saliculous acid do not present the characters of compounds of these elements with radicals; for the chlorine or bromine in them cannot be replaced by other elementary bodies. They may be considered as *saliculic acid* in which an equivalent of oxygen has been replaced by one of chlorine or bromine. In fact, they possess the characters of acids.

$C_{14}H_5O_5$	Anhydrous saliculic acid.
$\left.\begin{matrix}C_{14}H_5O_4\\ \hfill Cl\end{matrix}\right\}$	Chlorosaliculic acid.
$\left.\begin{matrix}C_{14}H_5O_4\\ \hfill Br\end{matrix}\right\}$	Bromosaliculic acid.
$3(C_{14}H_6O_2)+N_2$	Saliculimide.
$3(C_{14}H_5ClO_2)+N_2$	Chlorosaliculimide.

SALICULOUS ACID.

Syn. Saliculic Acid, Hyduret of Salicule, Hyduret of Spiroyle (Löwig). Discovered by Pagenstecher in the volatile oil of spiræa ulmaria; by Piria as a product of the decomposition of salicine. The latter ascertained its nature and composition. The identity of the two was rendered probable by Dumas, and proved by Ettling's analysis of the oil of spiræa.

To obtain it, the oil of spiræa is distilled with aqua potassa in excess as long as oil passes over. The residue, a solution of saliculite of potash, is supersaturated with dilute sulphuric acid, and again distilled, when saliculous acid distils over with the vapour of water. Or according to Piria: a mixture of 1 part of salicine, 1 part bichromate of potash, $2\frac{1}{2}$ of oil of vitriol, and 20 of water, is subjected to distillation. The salicine is dissolved in part of the water, the acid is diluted with the rest; the whole materials are then mixed in a retort, when heat is developed, and a gentle effervescence appears. When this is over, the distillation is commenced: $\frac{1}{2}$lb. salicine gives about 2 oz. of saliculous acid (Ettling). In both processes the distilled liquid contains saliculous acid, which separates from the water. It is purified by washing with water and rectification along with chloride of calcium.

Formula, $C_{14}H_5O_3 + aq.$

It is a colourless or pale-yellow, oily, inflammable liquid; sp. g. 1·1731; boiling at 370°, or, according to Piria, at 380°; becoming solid at $-4°$ (Löwig). It has a burning taste and a pleasant aromatic odour; is somewhat soluble in water, and mixes with alcohol and ether in all proportions. Its solution reddens litmus first, then bleaches it. Concentrated sulphuric acid decomposes it. When placed in contact with chlorine or bromine, 1 eq. hydrogen is removed, which forms hydrochloric or hydrobromic acids; and its place supplied by 1 eq. chlorine or bromine, producing chlorosaliculic and bromosaliculic acids. Saliculous acid, treated with excess of hydrate of potash, gives out hydrogen gas, while saliculic acid is formed. With potassium, hydrogen is also disengaged, while saliculite of potash is produced.

SALICULOUS ACID WITH BASES.

Saliculous acid combines with metallic oxides to form the saliculites, its basic water being replaced by 1 eq. metallic oxide. The salts of the fixed alkalies and ammonia are soluble, and possess an alkaline reaction. All the rest are insoluble. Most of them are yellow, and contain water of crystallization. A solution of the acid colours the salts of peroxide of iron purple: the colour disappears after a time. In acetate of copper it produces a green precipitate. All the saliculites are decomposed by the stronger acids, which separate the saliculous acid.

SALICULOUS ACID AND AMMONIA.

Saliculite of Ammonia.—Prepared by adding strong aqua ammoniæ to saliculous acid. A yellow solid mass, without taste, having a faint odour of roses; sparingly soluble with a yellow colour in cold water and alcohol, more readily dissolved by hot alcohol. By the cooling of a saturated solution transparent needles of a pale yellow are obtained. It is spontaneously decomposed if kept moist; becomes black, semifluid, and exhales ammonia with a penetrating smell of roses (Löwig). Dry saliculous acid easily absorbs dry ammonia; and the compound, according to Ettling, contains 3 atoms of the acid and 2 atoms of ammonia.

Saliculimide.— If saliculous acid be dissolved in three times its volume of alcohol, and ammonia added drop by drop, the liquid concretes into a solid paste of fine yellow needles. With the aid of a moderate heat these crystals dissolve; and the solution, if left to rest, deposits golden-yellow, brilliant, transparent prisms, which when dry are hard and pulverizable. Here 3 at. of the acid (or 1 at. considered as a tribasic acid) are acted on by 2 of ammonia, 6 at. of water being eliminated. The alcoholic liquid in which these crystals have formed is no longer able, even at a boiling heat, to dissolve them. They now require a threefold quantity of alcohol. This would indicate that at first saliculite of ammonia is formed, which by a longer contact with ammonia, and a slow separation of the crystals, passes into saliculamide. This body is decomposed by a high temperature. Heated with acids and alkalies, it is resolved into saliculous acid and ammonia. It is insoluble in water.

Formula, $C_{42}H_{18}O_6N_2$ (Ettling).

Saliculite of Potash; Neutral. — This is best obtained by adding saliculous acid to a warm solution of potash in alcohol, and allowing the whole to cool, when the salt separates almost pure in the form of four-sided pearly tables nearly colourless, very soluble in water, spontaneously decomposed by exposure to the air in a moist state. It contains water of crystallization, which is expelled by a heat of 212°. Formula, $2(C_{14}H_5O_3) + \left.\begin{matrix}KO\\HO\end{matrix}\right\}$. If the neutral salt be dissolved in hot alcohol, and saliculous acid added, an acid salt is deposited on cooling in yellowish-white, long, fine, and brilliant needles. When dry it becomes yellow at a temperature of 230°. Water decomposes it into saliculous acid, which separates, and neutral salt.

Saliculites of Soda, Lime, Baryta, and Magnesia may be formed directly. They have the properties of the potash salt. The salt of soda contains 2 at. of water of crystallization, expelled by a heat of 230°. There is likewise an acid salt of soda in fine shining needles. Saliculite of copper is anhydrous and green. The salts of zinc and mercury are yellow and insoluble.

Saliculite of Lead; Basic.—Saliculous acid is dissolved in weak alcohol, and acetate of lead added to the boiling solution. On cooling the salt is deposited, and is purified by boiling alcohol from any adhering acid. It is a lemon-yellow powder, which, when heated, froths up, giving off water and acid; insoluble in water. Its formula is $C_{14}H_5O_3 + 2PbO$. If saliculous acid be added to diacetate of lead, a yellow powder of the same composition is precipitated.

Saliculite of Silver.—According to Löwig, oxide of silver dissolves with apparent decomposition in an aqueous solution of saliculous acid; but this is denied by Ettling. A solution of nitrate of silver mixed with one of saliculite of potash, causes a greenish-yellow precipitate, which, when heated, is reduced without disengagement of gas, the vessel being silvered by the reduced metal.

PRODUCTS OF THE DECOMPOSITION OF SALICULOUS ACID.

MELANIC ACID.

Discovered by Piria. When saliculite of potash is exposed to the air, it acquires a green colour, which, after some time, becomes black. When no further change is perceived, the saliculous acid is completely converted into acetic acid and a black powder. The acetic acid thus formed is in the exact proportion to combine with all the potash contained in the original salt. The black powder possesses acid properties, and unites with bases; from which circumstance it has received its name.

The formula for melanic acid is $C_{10}H_4O_5$.

Three equivalents of oxygen and two of water unite with one atom of saliculite of potash, and convert its acid into one equivalent of acetic, and one equivalent of melanic acid.

SALICULIC ACID.

Discovered by Piria. This acid is prepared by heating saliculous acid with caustic potash. The mixture at first assumes a brown colour, but the heat must be continued until it is entirely white. At this time hydrogen is disengaged. The residue is to be dissolved in water and treated with a mineral acid, which separates the saliculic acid. In order to obtain it pure it must be repeatedly crystallized. Saliculic acid is likewise formed, when coumarine (stearoptene of the Tonka bean) is treated with potash in a similar manner.

Saliculic acid sublimes without decomposition, and may be thus obtained in the form of long crystalline needles, very similar in their appearance to benzoic acid. It crystallizes from water in fine tufts. This acid dissolves with difficulty in cold water, but very easily both in hot water and in alcohol. Sulphuric acid decomposes it when they are heated together.

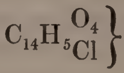
The formula of saliculic acid is $C_{14}H_5O_5 + H_2O$.

The salts of this acid have been little examined: its combination with oxide of silver is insoluble in water, and has the formula $C_{14}H_5O_5 + AgO$.

CHLOROSALICULIC ACID.

Syn. Chloride of Salicule, Chloride of Spiroyle. Dry chlorine gas is passed through anhydrous saliculous acid as long as hydrochloric acid is disengaged. On cooling, the compound becomes solid and crystalline. It is purified by crystallization out of a hot alcoholic solution, which deposits it on cooling in the form of pale yellow, oblique, rhombic tables, of a pearly lustre, having a peculiar aromatic odour, fusible and volatile without decomposition. It is inflammable, and burns with a green flame. It is insoluble in water, soluble in alcohol and ether. It combines with alkalies, and is separated from them unchanged by acids. Its solution in alcohol gives with acetate of copper a greenish-yellow, and with acetate of lead a yellow precipitate. Persalts of iron are tinged by it of a dark blue. When heated with potassium, it is decomposed with heat and light. Ammoniacal gas converts it into chlorosaliculimide.

This compound is distinguished from all analogous compounds of chlorine with compound radicals by its power of combining with bases, and of resisting the action of those bodies. It forms with metallic oxides peculiar salts, in which 1 at. chlorosaliculic acid is combined with 1 at. metallic oxide; so that they may be considered as compounds of saliculic acid with metallic chlorides $C_{14}H_5O_5 + MCl$, like the compounds of the chlorochromic acid with alkalies or metallic chlorides.

Formula of chlorosaliculic acid,  $C_{14}H_5\left.\begin{matrix}O_4\\Cl\end{matrix}\right\}$.

CHLOROSALICULIMIDE.

Formed by the action of ammonia on the preceding compound. Dry ammonia is passed over chlorosaliculic acid in a proper apparatus as long as water is formed. The new substance is left behind in a state of purity. It forms a solid deep-yellow mass, insoluble in cold water, decomposed by hot water, acids, and alkalies, with the formation of ammonia and chlorosaliculic acid. Three at. chlorosaliculic acid with 2 eq. ammonia produce 6 at. of water and 1 at. chlorosaliculimide, $C_{42}H_{15}O_{12}Cl_3 + N_2H_6 = 6HO + C_{42}H_{15}Cl_3N_2O_6$.

It hence appears to be saliculimide, in which 3 eq. hydrogen are replaced by 3 eq. chlorine.

BROMOSALICULIC ACID.

This compound, in its preparation, properties, and action with ammonia, is completely analogous to the preceding.

IODOSALICULIC ACID.

Saliculous acid dissolves iodine in great quantity, without apparent decomposition. But iodosaliculic acid may be obtained by distilling iodide of potassium with chlorosaliculic acid. It sublimes in the form of a dark-brown fusible mass, analogous in its relations to the two preceding compounds.

PRODUCTS OF THE DECOMPOSITION OF HYDURET OF SALICULE.

NITROSALICULIC ACID.

Saliculous acid, warmed with moderately strong nitric acid, is converted, with disengagement of nitrous acid, into a crystalline mass of nitrosaliculic acid, which is purified by washing with water, solution in alcohol, and crystallization. By spontaneous evaporation the alcoholic solution yields small transparent prisms of a golden-yellow colour, sparingly soluble in water. The solution stains the skin and nails permanently yellow, precipitates the salts of lead yellow, and those of copper green. It is inodorous, but has an acrid taste exciting cough. Heated with potassium, it is decomposed with explosion and fire. It combines with alkalies to form crystallizable compounds, which detonate when dried and heated. Ammonia colours the acid a deep blood-red. Chloride of iron is coloured cherry-red by it. These compounds demand a more accurate study.

Formula, $C_{12}H_3N_4O_{12}$.

Fuming nitric acid acts most violently on saliculous acid, producing a yellow matter which is volatile, and in the fixed residue a crystallizable substance not yet examined.

APPENDIX TO SALICULE.

VOLATILE OIL OF SPIRÆA ULMARIA.

According to the researches of Pagenstecher, this oil is not ready formed in the flowers, but is a product of the action of water during the distillation. The oil, as obtained, is yellow; and is a mixture of two, perhaps three, volatile oily substances, one of which has been described as saliculous acid, or hyduret of salicule. When the oil is exposed for some weeks to a cold of from 0°—4°, large transparent crystals of the acid separate, which melt at the ordinary temperature. The oil contains, besides, a substance like camphor, crystallizing in pearly scales, which are solid at the ordinary temperature. If the oil be mixed with aqua potassæ, the acid combines with potash, while the neutral oil is separated, and may be obtained by distillation. It is colourless, less volatile than water, and has, like the acid, the smell of the plant. It has not been further examined.

SALICINE.

Discovered by Le Roux and Buchner. It is found in the bark and leaves of all bitter willows: in salix helix, W. (salix monandra, Hoffm. salix purpurea, L.); also in salix amygdalina, L. (salix triandra,) &c. and in some species of poplar.

Dried or fresh willow bark is cut small, and exhausted by repeated boiling with water. The decoctions are concentrated, and, while boiling, treated with litharge till the liquid appears nearly colourless. The dissolved oxide of lead is removed, first by sulphuric acid, afterwards by sulphuret of barium, and, after the separation of the sulphuret of lead, evaporated, when salicine crystallizes; and is purified by repeated solution and crystallization (Merck). From willow bark which is fresh and rich in salicine, it may be obtained by cautious evaporation of the cold aqueous infusion (Merck). The oxide of lead removes from the solution gum, tannin, and extractive matter, which would impede the crystallization of the salicine. It also combines with the salicine, forming a kind of salt, which is decomposed by the sulphuric acid and sulphuret of barium. If the latter be carefully added, neither sulphuric acid nor baryta remain in the solution; and the sulphuret of lead, which separates, acts as a decolorizing agent.

Salicine crystallizes in white, transparent, or inodorous, silky needles and laminæ, very bitter, and permanent in the atmosphere. It has a bitter taste, and does not act on vegetable colours. At 212° it loses no weight; it melts at 230°, and is decomposed at a higher temperature, becomes yellow, resinous in appearance, and gives off vapours which burn with a bright flame, leaving a voluminous coal, which when burned leaves no residue. Salicine dissolves in 5·6 parts of water at the ordinary temperature, and to any extent in boiling water. It is soluble in alcohol, but not in ether or fixed oils. It is not precipitated by any reagent. It dissolves in strong sulphuric acid with a blood-red colour, by which character its presence in the willow bark may be recognized. It yields, when acted on by nitric acid, much carbazotic acid. Hydrochloric acid and dilute sulphuric acid change it into a white, tasteless powder insoluble in water, (*saliretine*,) soluble in alkalies and alcohol, from which it is again precipitated by acids and water. The liquid in which saliretine has been formed contains grape sugar. (Piria.) Subacetate of lead does not precipitate salicine till ammonia be added, when a white precipitate appears.

Formula of salicine, $C_{42}H_{29}O_{22} = C_{42}H_{23}O_{16} + 6$ aq.

Distilled with bichromate of potash and sulphuric acid, salicine yields formic acid, carbonic acid, and saliculous acid. Treated with chlorine, chlorosalicine is produced.

Rutiline.—Braconnot has thus named the product of the decomposition of salicine by strong sulphuric acid. When pure, it is brownish-red, with a tinge of yellow while moist, dark-brown when dry; brittle, tasteless, insoluble in water and alcohol. Strong acids colour it of a fine blood-red; alkalies of a deep violet.

PRODUCTS OF THE DECOMPOSITION OF SALICINE BY ACIDS AND CHLORINE.

SALIRETINE.

The white precipitate obtained when salicine is boiled in dilute muriatic or sulphuric acid is saliretine. It may be obtained either anhydrous or as a hydrate. The remaining constituents of the salicine, which do not enter into the constitution of this body, form grape sugar. Saliretine is insoluble in water and ammonia, but soluble in alcohol, ether, concentrated acetic acid, and caustic alkalies. It is precipitated from its solution in alkalies by acids, and from alcohol, ether, and acetic acid, by simple dilution with water. It acquires a blood-red colour when in contact with sulphuric acid; nitric acid converts it to carbazotic acid.

The formula of saliretine is $C_{30}H_{16}O_8 = C_{30}H_{15}O_7 +$ aq. One atom of salicine is decomposed by acids into 1 at. saliretine and 1 at. grape sugar, $C_{30}H_{16}O_8 + C_{12}H_{14}O_{14} = C_{42}H_{29}O_{22}$.

CHLOROSALICINE.

Discovered by Piria. A solution of salicine in water becomes turbid, when chlorine gas is conducted through it. A crystalline yellow powder is deposited, which dissolves with difficulty in water, but very easily in hot alcohol. Its formula is $C_{42}H_{25}Cl_4O_{22}$; it may be represented as salicine, in which 4 equivalents of hydrogen are replaced by 4 eq. of chlorine. When the solution of salicine is heated to 60° C. during the saturation with chlorine, a compound is obtained, containing much more chlorine than the last-mentioned substance, in the form of a red thick oil, heavier than water. It is soluble both in alcohol and alkalies; insoluble in water and acids.

Its formula is $C_{42}H_{18}Cl_7O_{18}$.

PHLORIDZINE.

Discovered by De Koninck in the fresh bark of the root of the apple, pear, cherry and plum tree. In its composition and all its characters it is closely connected with salicine, and may be considered as crystallized salicine + 2 at. of oxygen.

Formula, $C_{42}H_{29}O_{24} = C_{42}H_{23}O_{18} + 6$ aq.

It is extracted from the bark by boiling alcohol of 80 p. c. The alcohol is distilled off, and the phloridzine crystallizes out of the residual liquid.

It forms fine, colourless, four-sided silky needles, soluble in 1000 parts of cold water, and in every proportion in boiling water. The solution has a bitter, slightly astringent taste. It is soluble in alcohol, and sparingly soluble in ether. Sp. g. 1·4298. At 212° it loses 4 at. water of crystallization, it melts at 300°, and is decomposed at 384°. A solution of phloridzine gives with subacetate of lead a white precipitate, which, according to Mulder, is 1 at. of anhydrous phloridzine combined with 6 at. of oxide of lead.

Phloridzine is acted on by dilute acids exactly as salicine is. Both substances have been used with success in intermittents.

PRODUCTS OF THE DECOMPOSITION OF PHLORIDZINE.

PHLORETINE.

Discovered by Stass. When a solution of phloridzine in water is boiled with the addition of a little muriatic or sulphuric acid, it is converted in a manner precisely similar to salicine, into grape sugar and phloretine. This differs from saliretine by containing two atoms of oxygen more than that substance. Phloretine crystallizes in plates, of a sweet taste, slightly soluble in water and in ether, very soluble in alcohol, concentrated acetic acid, alkalies, sulphuric acid, and muriatic acid.

Its formula is $C_{30}H_{15}O_{10}$.

PHLORIDZEINE.

Discovered by Stass. When phloridzine is moistened with ammonia and exposed to the atmosphere, it acquires a blue colour, by the absorption of oxygen, and may be dissolved in an excess of ammonia. A red powder is precipitated from the solution on the addition of acids, which is the substance named phloridzeine. Its formula is $C_{42}H_{29}O_{26}N_2$. It arises from phloridzine, by the separation of 6 atoms of water, and combination of 8 atoms of oxygen, and 2 equivalents of ammonia. Its solution in ammonia gives by evaporation a purple red mass, the surface of which has the metallic lustre and colour of copper. It remains unchanged in the air, is easily soluble in water, forming a solution of splendid blue colour. Sulphuretted hydrogen and other substances, which have an attraction for oxygen, decolorize it, but the colour is restored on exposure to air, by the absorption of oxygen.

CINNAMULE.

The hypothetical radical of oil of cinnamon and of cinnamic acid. According to the researches of Dumas and Peligot, Ceylonese oil of cinnamon is composed according to the formula $C_{18}H_8O_2$; and by absorbing 2 at. oxygen from the atmosphere is converted into cinnamic acid. Oil of cinnamon forms with nitric acid a compound which crystallizes in oblique rhombic prisms, consisting of an equal number of atoms of oil of cinnamon, nitric acid, and water. With hydrochloric acid it forms a green solid mass, composed of an equal number of equivalents of the anhydrous oil and of hydrochloric acid. With ammonia it forms a solid friable mass, also composed of one equivalent of each substance.

Formula of cinnamule, $C_{18}H_7O_2$: Symbol, Ci.

Chlorine decomposes the oil of cinnamon; forming a liquid compound, and another which sublimes in long white needles. The latter has the formula $C_{18}H_4Cl_4O_2$; and consequently it is oil of cinnamon in which half the hydrogen has been replaced by its equivalent of chlorine. There is here some analogy with the compounds of benzule; but there are also great differences, which may be explained by the fact, that, according to Blanchet and Sell, the oil of cinnamon consists of two distinct oils, one heavier, and one lighter than water. The heavier has at 77° a sp. g. of 1·008, and boils at 430°. If the commercial oil be treated with barytic water, a saline combination of the heavy oil is produced, which is soluble in water, and from which the heavy oil is separated by acids. The lighter oil may be distilled from the mixture of the commercial oil with baryta.

According to a late investigation by Mulder, the composition of the oil of cinnamon of Ceylon, Java, and China, and the oil of cassia flowers and cassia bark, is represented by the formula $C_{20}H_{11}O_2 = 1$ eq.: the combination with hydrochloric acid contains 1 eq. of that acid; that with ammonia 1 eq. ammonia. The oil of cassia flowers combines only with half as much ammonia. Blanchet's analysis of Ceylon oil of cinnamon gave a result closely approximating to that of Mulder; but Dumas, on repeating his earlier analyses, found reason to dispute the correctness of Mulder's formula. As the difference in the percentage of hydrogen in the analyses of Dumas and Mulder is above 1 per cent. which cannot arise from an error in the manipulation, we are led to consider the existence of two oils as highly probable; and new researches, conducted with the utmost care, are necessary to clear up these difficulties and contradictions. In the mean time it may be considered as certain, that the oil which forms with nitric acid the crystalline compound above-mentioned, has the formula $C_{18}H_8O_2$. (Dumas.)

OIL OF CINNAMON OR CASSIA.

Obtained by distilling the bark of laurus cinnamomum, and the bark and flowers of cassia. It is a yellow oil, heavier than water, possessing the odour of cinnamon, solid below 32°, melting at 23°. It has a pungent, burning, sweetish taste; deposits crystals when kept, and when exposed to the air becomes brown, and passes into cinnamic acid. It is sparingly soluble in water, forming cinnamon water. This solution, mixed with iodine and iodide of potassium, yields brilliant reddish-brown crystals of a strong metallic lustre; the probable composition of which, according to Apjohn, is $KI + I_3CiH = KI + (C_{18}H_7O_2 + H) + I_3$, corresponding in 100 parts to 12·26 iodide of potassium, 28·08 iodine, and 59·66 oil of cinnamon. To obtain these crystals, 240 grains of iodide of potassium, and 10 grains of iodine, dissolved in a little water, are added to 2 lbs. of cinnamon water, and the mixture exposed to a temperature of 32°, when the crystals form. They are soluble in ether and alcohol without alteration, but are decomposed by water. (Apjohn.)

Aqua potassæ dissolves oil of cinnamon easily and completely, and diluted acids separate it again unchanged from the solution. If the solution of the oil in potash be distilled, an oil passes over with the vapour of water, which is lighter than water, has an odour of cinnamon and bitter almonds, and is composed according to the formula $C_{18}H_{10}O_2$: the residue contains benzoate of potash, mixed with a black matter. (Mulder.) Oil of cinnamon, heated with hydrate of potash, gives off hydrogen gas. All these decompositions are as yet unexplained. The oil, if mixed with nitric acid in the cold, becomes thick, and is wholly or partially converted into a crystalline mass. If boiled with nitric acid, the smell of oil of bitter almonds is perceived, and benzoic acid is found in the residue. Benzoic acid is also formed by the action of hypochlorites on the oil of cinnamon. Ammoniacal gas solidifies the oil, producing undoubtedly several bodies; one of which is soluble in alcohol and ether, and crystallizes in fine silky needles grouped together. The composition of these substances has not been examined.

CINNAMIC ACID.

Discovered by Dumas and Peligot. It is formed in hard translucent prisms, when oil of cinnamon is long exposed to the atmosphere. It may also be easily obtained by dissolving in potash the oil of balsam of Peru (see that article) with a gentle heat, evaporating to dryness, dissolving the residue of cinnamate of potash in boiling water, and adding an excess of hydrochloric acid; the cinnamic acid crystallizes on cooling, and is purified by repeated crystallization. Colourless, transparent scales, having a weak aromatic taste; less soluble in hot and cold water than benzoic acid. It crystallizes from alcohol in colourless rhombic prisms, which are hard and friable, fusible at 240°, boiling at 555°, and distilling as a heavy oil, which consolidates on the neck of the retort to a white crystalline mass. By the action of nitric acid it is converted into hyduret of benzule, and a crystallizable acid which has very nearly the same composition as benzoic acid, but is easily distinguished from that acid by its salts. The probable formula of this new acid is $C_{15}H_5O_3$. (Plantamour.) This reaction is unexplained.

The formula of anhydrous cinnamic acid is $C_{18}H_7O_3$: Symbol, CiO.

SALTS OF CINNAMIC ACID.

Cinnamic acid forms with metallic oxides salts which, in general, are analogous to the benzoates. In these salts 1 at. of basic water in the acid is replaced by the oxide. Cinnamate of silver, obtained by mixing a solution of neutral cinnamate of potash with nitrate of silver, is a white, flocculent, amorphous precipitate, which becomes black in boiling water.

HYDURET OF CINNAMULE.

Discovered by Dumas and Peligot. Obtained by putting freshly prepared nitrate of hyduret of cinnamule in contact with water, when the nitric acid combines with the water, and the hyduret of cinnamule separates. It is an oily liquid, which, if again placed in contact with nitric acid, solidifies instantly and completely. It seems to be the chief ingredient in oil of cinnamon.

Formula, $C_{18}H_8O_2$, or $C_{18}H_7O_2 + H$: Symbol, CiH.

CHLORINE AND OIL OF CINNAMON.

The action of chlorine on Chinese oil of cinnamon gives rise to several new products. Heat is developed, much hydrochloric acid gas is given off; the oil becomes at first brown, afterwards colourless, and thickens. If the oil be distilled in a stream of chlorine, the portion which first passes over is colourless, very fluid, and instantly converted by liquor potassæ into a soluble crystalline mass. This fluid oil may be mixed with sulphuric acid without decomposition. If left to itself for some time, it solidifies into a crystalline mass, which seems to be benzoic acid. After this fluid oil, there distils a brown oil, which possesses in a less degree the same property, and when treated with liquor potassæ leaves undissolved an oily body containing chlorine. If the products of this distillation are repeatedly exposed to the action of chlorine at a high temperature, there are at last obtained a black coaly residue, and a volatile white crystalline substance, which is very fusible, and unaltered by oil of vitriol, or by distillation in ammoniacal gas. Its formula is $C_{18}H_4Cl_4O_2$. Dumas and Peligot have named it Chlorocinnose.

APPENDIX TO THE COMPOUNDS OF CINNAMULE.

OIL OF BALSAM OF PERU.

The balsams of Peru and Tolu contain compounds which belong to the series of cinnamule.

According to Stoltz and Wernher, 2 vol. of balsam of Peru, and 3 vol. of aqua potassæ sp. g. 1·300, when heated together, produce a yellow or yellowish-brown oil (oil of balsam of Peru,) which swims above a dark brown or black syrupy liquid, soluble in water, which contains all the potash.

The former is purified by distillation, leaving a slightly carbonaceous residue. It is then clear and colourless. Fremy calls it Cinnameine; its probable formula is $C_{144}H_{65}O_{20}$. According to Plantamour and Fremy, this substance, which is allied to the fat oils, when boiled with alkalies, produces cinnamic acid, which combines with the alkali, and a neutral substance, just as in the saponification of fat oils. The latter substance is peruvine. When a solution of the oil of Peru balsam in alcohol is mixed with an alcoholic solution of potash, it instantly solidifies into a micaceous mass of cinnamate of potash. After the alcohol has been distilled off by the application of a gentle heat, the alkaline residue by distillation with water yields at first a clear and colourless oil, heavier than water, which from its reactions and composition appears to be cinnamic ether (cinnamate of oxide of ethule), the production of which in these circumstances is very remarkable. The latter product of the distillation is peruvine.

Peruvine is a colourless oily fluid, lighter than water, refracting light powerfully. Its composition approaches to $C_{36}H_{25}O_4$. According to this formula, 1 at. cinnameine produces 3 at. cinnamic acid, and 1 at. peruvine.

When dry hydrate of potash is employed instead of the aqueous or alcoholic solution of potash, the cinnameine is decomposed in a different manner. Hydrogen gas is given off, while cinnamate of potash is formed.

When cinnameine is exposed to a cold of + 26°, it deposits neutral crystals, soluble in alcohol and ether, the formula of which is $C_{18}H_8O_2$, exactly that of hyduret of cinnamule. This substance, therefore, is isomeric with hyduret of cinnamule, as benzoine is with hyduret of benzule.

Cinnameine, mixed with oil of vitriol, is converted into a brown, resinous matter, which appears to be a compound of 1 at. cinnameine and 7 at. water.

By the action of chlorine, cinnameine is converted into chloride of benzule, and an oily fluid, containing no chlorine, which cannot be separated from it.

Tolu balsam, or balsam of Tolu, contains the same compounds as balsam of Peru. (Fremy.) All these substances and their decomposition demand a more accurate and minute investigation.

According to Richter, the oil of balsam of Peru consists of two distinct oils, which may be separated by agitation with 2 vol. of alcohol at 75 p. c. The oil soluble in such alcohol he calls Myriospermine; the other, which is insoluble, Myroxiline.

Myroxiline.—Richter dissolves in absolute alcohol the brown oil left after continued agitation with weak alcohol, and exposes the solution in weak alcohol to the freezing temperature, whereby some of the brown oil separates, which is added to the solution in absolute alcohol. This solution, mixed with water, is now left to spontaneous evaporation, when the myroxiline at the temperature of 42° crystallizes in tallowy masses grouped in a circular form. The specific gravity of myroxiline is 1·111. By the action of liquor potassæ it produces cinnamic acid and a resinoid substance.

Myriospermine.—The spirituous solution containing the myriospermine being evaporated, that substance is left as an oil nearly colourless, possessing a great refracting power. It crystallizes from a concentrated solution in alcohol of 75 p. c. at the temperature of from + 14° to + 3°, in fine needles grouped together, which contain alcohol. According to Richter, myriospermine is converted by the action of an alcoholic solution of potash into an acid, which differs from cinnamic acid essentially in its capacity of saturation. The atomic weight of this acid, in its compound with oxide of silver, according to him is 1553·85 (0 = 100·00). (Richter in Erdmann's Journal, t. xiii. p. 175.)

II. RADICALS FORMING BASES.

ETHULE.

Ethule is the hypothetical radical of the ethers. It has not yet been obtained in a separate form. With 1 eq. oxygen ethule forms ether, the oxide of ethule, which possesses the properties of a base. Alcohol is the hydrate of oxide of ethule. The formula of ethule is C_4H_5: Symbol, Ae.

ETHULE AND OXYGEN.

Oxide of Ethule; Ether. Formula, C_4H_5O: Symb. AeO. Syn. Sulphuric Ether. A mixture of ether and alcohol seems to have been known even in the thirteenth and fifteenth centuries. But Valerius Cordus first published, in 1544, precise directions for making ether, according to which a mixture of equal weights of alcohol and oil of vitriol is to be distilled; a process still frequently employed. The preparation of ether seems after this to have sunk into oblivion, till Frobenius in 1729 anew described it.

Ether is formed by the decomposition of the bisulphate, biphosphate, and binarseniate of oxide of ethule, (sulphovinic, phosphovinic, and arseniovinic acids,) and by the action of fluoride of boron, chloride of zinc, chloride of tin, and other chlorides, on alcohol.

Prep.—Five parts of alcohol of 90 p. c. are mixed with 9 parts of oil of vitriol in a vessel of copper or iron placed in cold water. The mixture is now introduced into a still, and by means of a strong fire is kept in a state of continued ebullition. The vapour of ether distils along with those of water and alcohol, and all are condensed in an efficient cooling apparatus. A quantity of alcohol of the same strength, equal in bulk to the liquids distilled off, is to be added to the liquid in the still, and the operation repeated. To the distilled liquid is now added so much of an alcoholic solution of potash as causes a perceptible alkaline reaction; and it is then rectified by distillation in the water-bath as long as the ether, which distils over, has a sp. g. of 0·720 to 0·725 at 80° F. Or before rectification it may be mixed with a little milk of lime and its own bulk of water. By allowing it to stand for some days over chloride of calcium, or quicklime, and a new rectification in contact with one of these substances, it is obtained perfectly pure.

On the large scale, a given quantity of oil of vitriol may be made to convert an almost unlimited quantity of alcohol into ether. The mixture of oil of vitriol and alcohol of 90 p. c. as above, being introduced into the retort or still, is connected with a vessel full of the same alcohol by means of a syphon tube, furnished with a stop-cock, and passing through the tubulure of the retort. The longer limb of the syphon is so arranged as just to dip into the liquid in the retort. As soon as full ebullition is going on, the stop-cock is opened, so as to allow alcohol to flow into the retort in such a manner as to keep the boiling liquid exactly at the same level; that is, to supply a volume of alcohol equal to that of the liquid which distils over. If the operation be well managed, the whole of the alcohol which enters the retort passes off as ether and water, and the oil of vitriol continues for a long time to produce this decomposition without losing any of its power. In fact, it would continue to do so for an indefinite time, were it not that it is gradually diluted by the superfluous water contained in alcohol of 90 p. c.; and when diluted to a certain degree, it can no longer produce ether. For the explanation of what takes place in this interesting process, see below (Products of the decomposition of bisulphate of oxide of ethule or sulphovinic acid).

Ether is a colourless, clear, and very mobile liquid; and has the sp. g. 0·7119 at 75°, 0·7154 at 68°, and 0·7237 at 55°. It refracts light strongly, is a non-conductor of electricity, boils at 96°, and freezes at from $-24°$ to $-45°$. By its evaporation an intense cold is produced. It has a pleasant, penetrating, ethereal odour; its taste is cooling (from its quick evaporation), penetrating, and aromatic. It is highly inflammable; and its vapour, mixed with oxygen or atmospheric air, forms a very dangerous explosive mixture. It dissolves in 10 parts of water, and is miscible with alcohol and the fatty and volatile oils in all proportions. When kept in vessels containing air, ether, by absorption of oxygen, is partly converted into acetic acid and water, and becomes acid to test paper. This latter effect is also sometimes owing to the presence of sulphurous acid, which gradually passes into sulphuric acid, or which proceeds from the decomposition of a little oil of wine which has distilled over with it.

At a higher temperature ether rapidly absorbs oxygen, producing acetic, formic, and lampic (aldehydic) acids; the last of which is known by its suffocating smell, and its power of causing a flow of tears from the eyes. When passed through a red-hot glass tube, ether is resolved into aldehyde, olefiant gas, and marsh gas (light carburetted hydrogen). Ether dissolves $\frac{1}{80}$th of sulphur and $\frac{1}{37}$th of phosphorus. Bromine and iodine are dissolved by it in quantity, but with decomposition ; hydrobromic and hydriodic acids are produced, along with other products not yet examined. Chlorine gas, passed through ether, instantly decomposes it ; at the ordinary temperature each bubble inflames, while hydrochloric acid and carbon are produced. If the ether be cooled, there is formed, besides hydrochloric acid, a fluid compound, containing chlorine, which with potash produces chloride of potassium and acetate of potash. (Malaguti.) Anhydrous sulphuric acid decomposes ether in two ways. In the cold are produced isæthionic and althionic acids, sulphate of oxide of ethule, oil of wine, and bisulphate of oxide of ethule. But if heat be employed, these products are decomposed ; and sulphate of oxide of ethule, oil of wine, water, and ether, accompanied by acetic, formic, and sulphurous acids, carbonic oxide, and olefiant gas, distil over.

Nitric acid, with the aid of heat, converts ether into aldehyde, with acetic, formic, oxalic, and carbonic acids. If oxygen from nitric acid be added to the elements of ether, we obtain

Oxygen	1 at. ether = C_4H_5O.
from 2 atoms	1 at. aldehyde, and 2 at. water.
4 atoms	1 at. acetic acid, and 2 at. water.
8 atoms	2 at. formic acid, and 3 at. water.
10 atoms	2 at. oxalic acid, and 5 at. water.
12 atoms	4 at. carbonic acid, and 5 at. water.

Hydrochloric acid is greedily absorbed by ether ; and the concentrated solution when distilled yields chloride of ethule. Anhydrous alkalies have no action on pure ether at the ordinary temperature : but if water and air are present, the ether becomes brown ; and after some time the alkali is found to be in part combined with acetic and formic acids, formed by oxidation. The brown substance appears to be formed by the decomposition of aldehyde.

Potassium and sodium decompose ether by depriving it of oxygen, although slowly and imperfectly. There are formed in this reaction gaseous and oily carbo-hydrogens. The oxides of potassium and sodium when formed combine with undecomposed ether, forming saline compounds. Lead, zinc, and iron, when in contact with ether, cause the absorption of oxygen and the production of acetates of the metallic oxides.

Oxide of ethule (ether) combines with water to form alcohol (hydrate of oxide of ethule); and with acids, forming neutral and acid salts. The acid salts are commonly named acids, as sulphovinic and phosphovinic acids; the neutral salts are called compound ethers, as oxalic ether, &c.

Ether is used in medicine: internally as a diffusible stimulant; externally to produce cold by its evaporation, and also in frictions. In pharmacy it is also sometimes employed as a solvent for phosphorus, sulphur, iodine, sesquichloride of iron and ammonia. It is the best solvent of the fixed oils.

Pure ether should be clear and colourless, neutral to test paper, and of sp. g. not more than 0·73 at 68° for medical use. It should not become milky when mixed with water, and should not dissolve in less than 10 parts of water.

OXIDE OF ETHULE WITH WATER.

Alcohol. Hydrate of oxide of ethule. Formula, $C_4H_6O_2$: Symbol, $AeO + HO$, &c. &c.

Alcohol is formed by long contact between ether and water, which combine very slowly; but these substances combine instantly when presented to each other in the nascent state. This takes place, for example, when the acid salts of oxide of ethule are heated with water; when the neutral salts of oxide of ethule, or the haloid salts of ethule, are decomposed by being heated with the hydrated alkalies; when the double salts of oxide of ethule with lime or baryta are gently heated; and in the peculiar decomposition of sugar which constitutes the vinous fermentation.

By the distillation of all liquids which have undergone the vinous fermentation there is obtained a more or less diluted alcohol, the strength of which is indicated by its specific gravity. A liquid containing 50 to 52 per cent. of alcohol is called spirits (brandy, &c.): its sp. g. is 0·95 or 0·94. Rectified spirit of wine contains from 66 to 70 per cent.; and has a sp. g. of 0·89 to 0·88. The most highly rectified spirit of wine, the sp. g. of which is 0·835 to 0·840, contains about 90 per cent. of alcohol. All these specific gravities are referred to a temperature of 60°.

Absolute alcohol is obtained by saturating spirits of 90 per cent. with fused chloride of calcium, and distilling the solution; the water remains behind in combination with the chloride of calcium. Quicklime, and dry carbonate of potash, may be employed for the same purpose. According to Graham, alcohol of 90 p. c. is placed under the exhausted receiver of the air-pump near a vessel containing quicklime. In the course of a few days the alcohol is deprived of the water which it contains. Lastly, alcohol of 90 per cent. is placed in a bladder, which is suspended in a warm place. The water moistens the bladder, and evaporates from the external surface, while the alcohol is left. In this way it may be brought to 98 per cent.; but with some loss, as alcohol escapes through the upper part of the bladder, which is not in contact with the liquid.

Alcohol, as obtained from brandy or whisky, has a peculiar odour, derived from the presence of an essential oil. This is best removed on the small scale by rectification with a little caustic potash (Göbel, Liebig), or by digesting the spirits with freshly ignited pine charcoal.

Pure alcohol is a clear, colourless, mobile liquid; sp. g. 0·792—0·791 at 68°, or 0·7947 at 60°. It boils at 172°, and has not been frozen by any cold hitherto produced. It refracts light powerfully, and is a non-conductor of electricity. The odour of alcohol is agreeable and penetrating, and it intoxicates powerfully. It is highly inflammable, and its combustion with a sufficient supply of oxygen yields only carbonic acid and water. If the supply of oxygen be deficient, it burns with a smoky flame. Alcohol greedily absorbs water from the atmosphere; and deprives animal substances of the water they contain, causing them to shrivel up. Hence its use in preserving anatomical preparations. Water and alcohol unite with disengagement of heat. Snow mixed with alcohol produces an intense cold. Great condensation attends the combination of alcohol and water. When 1 at. alcohol and 6 at. water are mixed, the bulk of the liquids contracts from 103·735 to 100 measures. Sp. g. of this mixture 0 920 at 60°. The boiling point of a mixture of alcohol and water rises with the proportion of water within certain limits. Alcohol of 94 p. c. has the same boiling point as pure alcohol; but alcohol from 96 to 99 p. c. boils at a somewhat lower temperature. Hence in the preparation of absolute alcohol, the first portions which distil contain water, and are followed by absolute alcohol. For the percentage of alcohol in spirits of different densities, see the Table in the Appendix.

The purity of alcohol is known by its specific gravity. It should contain no essential oil, which may be detected by the addition of colourless oil of vitriol, which causes a red tinge if oil be present. According to Vogel, nitrate of silver is a still more delicate test for the oil, as when added to alcohol contaminated with this oil, and exposed to the sun's rays, it soon turns red; while no such effect is produced with pure alcohol. Alcohol should be neutral to test paper, and should leave no residue whatever on evaporation.

Alcohol, in the form of rectified spirit of wine, and proof spirit (equal volumes of alcohol at 90 p. c. and water), is extensively used in pharmacy, for the preparation of tinctures, spirits, &c. It is also employed as a powerful solvent for resins, oils, and vegetable alkalies, and in the preparation of ether and its compounds.

In the form of brandy and other ardent spirits, and of wine, it is much employed in medicine as a powerful diffusible stimulant, especially in diseases of a typhoid character.

ALCOHOL AND AMMONIA.

Alcohol absorbs ammoniacal gas readily. The alcohol ammoniatum of the pharmacopœia contains such a mixture, which is made by adding aqua ammoniæ to alcohol.

ALCOHOL AND IODINE.

Alcohol readily dissolves iodine, forming a dark brown solution,—tincture of iodine. The addition of water to the tincture causes nearly the whole of the iodine to separate in crystalline scales. Tincture of iodine is used in medicine; and, being a very powerful remedy, must be employed with caution.

ALCOHOL AND POTASH.

Alcohol dissolves caustic potash in the cold, and furnishes a method of purifying it from carbonate and sulphate, and chloride of potassium, all of which are left undissolved by the alcohol. If the alcoholic solution of potash be exposed to the atmosphere and warmed, it becomes brown, and is found to contain a substance apparently identical with resin of aldehyde, while acids, probably the acetic, formic, and aldehydic, are formed, and unite with the potash. When a mixture of equal parts of caustic lime and potash, moistened with alcohol, is subjected to distillation, pure hydrogen gas is evolved, and an acetate remains in the residue. (Dumas.)

ALCOHOL AND SALTS.

Alcohol dissolves many salts. Of inorganic salts, all those that are deliquescent in the atmosphere, with the exception of carbonate of potash, are soluble in alcohol. According to Graham, absolute alcohol combines with many salts, forming crystallizable compounds, which he calls alcoates, in which the alcohol performs functions analogous to those of hydratic (basic) water, and water of crystallization. These compounds are very easily decomposed.

Most of the organic acids are soluble in alcohol; and many of the salts which these acids form with inorganic bases, even those that are not deliquescent, dissolve easily in alcohol. Some of these solutions are used in medicine; as tincture of soap, and opodeldoc, which is a solution of hard soap in alcohol.

A mixture of alcohol and ether is used in medicine, under the name of spiritus vini æthereus.

Acids decompose alcohol; the oxygen acids by combining with the ether, the hydrogen acids by decomposing it. In the former case, acid salts of ethule are formed; in the latter, compounds of ethule with the radical of the acid. Potassium and sodium decompose the water of the hydrate of oxide of ethule (alcohol); combining with its oxygen, and disengaging hydrogen gas. The potash and soda which are formed produce crystallizable compounds with the oxide of ethule (ether).

ETHULE AND CHLORINE.

Chloride of Ethule. Syn. Hydrochloric or Muriatic Ether.—This compound is formed whenever alcohol is brought in contact with hydrochloric acid; and also by the action of many easily decomposed metallic chlorides, as sesquichloride of antimony, bichloride of tin, &c. on alcohol. In the latter cases, aldehyde is produced along with chloride of ethule. It is best prepared by saturating alcohol with hydrochloric acid gas, and distilling in the water-bath. The distilled liquid is collected in a receiver carefully cooled, and purified from alcohol and water by means of chloride of calcium. It must be preserved in stoppered bottles which are inverted.

Chloride of ethule is a colourless liquid, having a penetrating aromatic odour, somewhat resembling that of garlic. It has the sp. g. 0·874 at 40°, boils at 51°, is neutral, dissolves in 24 parts of water, does not precipitate nitrate of silver, and when kindled burns with a luminous flame edged with green, producing vapours of hydrochloric acid. Passed through a red-hot tube, it is resolved into equal volumes of hydrochloric acid and olefiant gases. Its vapour, mixed with chlorine, and first kept for 24 hours in the dark, then exposed to the sun-light, produces chloride of carbon (C_4Cl_6) and hydrochloric acid. (Laurent.) If left long in contact with hydrated alkalies, it produces chloride of the metal, and hydrate of oxide of ethule (alcohol).

Formula of the chloride of ethule, C_4H_5Cl, or AeCl.

BROMIDE OF ETHULE.

Syn. Hydrobromic Ether.—Discovered by Serullas. One part of bromine is dissolved in 4 of alcohol, and the solution being introduced into a tubulated retort, connected with a good cooling apparatus, a quantity of phosphorus, equal to $\frac{1}{8}$ of the weight of the bromine, is added. After the heat produced by the solution of the phosphorus has subsided, the liquid is distilled with a very gentle heat. Water added to the distilled liquid causes the bromide of ethule to separate. It is a colourless and very volatile liquid, having a penetrating ethereal smell and taste; heavier than water, miscible with alcohol and ether in every proportion. It is not decomposed by contact with water.

Formula, C_4H_5Br, or AeBr.

IODIDE OF ETHULE.

Syn. Hydriodic Ether.—Discovered by Gay-Lussac. Obtained by saturating alcohol with hydriodic acid and distilling; or by the use of iodide of phosphorus, like the preceding substance.

It is a colourless liquid, of a penetrating ethereal smell, boiling alone at 160°; but, when heated along with water, its temperature does not rise beyond 150°. Its density at 70° is 1·92. It takes fire with difficulty. Its vapour, passed through a red-hot tube, is resolved into charcoal, iodine, and a new substance which contains iodine and carbon, is not very volatile, and is insoluble in water, acids, and alkalies. This liquid has not yet been sufficiently examined.

Formula of iodide of ethule, C_4H_5I, or AeI.

When the bromide and iodide of phosphorus are employed to produce the two last substances, the phosphorus is oxidized at the expense of the oxide of ethule, while the ethule combines with the bromine or iodine: 3 at. alcohol, and 1 at. sesquibromide of phosphorus, for example, yield 1 at. hydrated phosphorous acid, and 3 at. bromide of ethule. $3AeO,HO + P_2 = Br_3 3AeBr + P_2O_3, 3HO$.

SULPHURET OF ETHULE.

Sulphuret of ethule is obtained, according to Regnault, when chloride of ethule is conducted in the gaseous form through a solution of protosulphuret of potassium in alcohol. After some time, chloride of potassium is separated, and the liquid contains sulphuret of ethule, which may be precipitated by the addition of water. Sulphuret of ethule has a disagreeable penetrating odour, similar to that of garlic: its specific gravity is 0·815; it boils at 153°. Its formula is $C_4H_5S = AeS$.

HYDROSULPHURET OF SULPHURET OF ETHULE.

Syn. Mercaptan.—Discovered by Zeise. To prepare this remarkable compound, aqua potassæ of sp. g. 1·28 is first saturated with sulphuretted hydrogen gas, and thereby converted into a strong solution of hydrosulphuret of sulphuret of potassium. It is then distilled along with an equal volume of a solution, of the same density, of the double sulphate of oxide of ethule and lime (sulphovinate of lime). The operation is performed in the water-bath, and the receiver is carefully cooled. The distilled liquid is purified from any free sulphuretted hydrogen that may be present by digestion and rectification with a little red oxide of mercury, and from water and alcohol by digestion with chloride of calcium.

Mercaptan is formed also, according to Regnault, when chloride of ethule and a solution in alcohol of the combination of sulphuret of potassium with sulphuretted hydrogen are brought together.

Mercaptan is a clear, colourless, mobile, ethereal liquid, possessing a very strong penetrating disagreeable odour, resembling that of garlic or assafœtida. It boils at about 98° (according to Zeise, at 144°); has the sp. g. 0·842 at 60°; is very inflammable, burning with a blue flame, and is neutral to test paper. It is sparingly soluble in water, miscible with alcohol and ether in all proportions. At a very low temperature it congeals into a foliated crystalline mass. It dissolves sulphur, phosphorus, and iodine.

Its empirical formula is $C_4H_6S_2 = AeS + HS$.

The chemical relations of mercaptan correspond to its constitution. It is alcohol, in which the oxygen has been replaced by sulphur; or it is the compound of ethule with sulphur, corresponding to alcohol, in which ethule is combined with oxygen. Thus—

Alcohol = Hydrate of oxide of ethule . . . = $AeO + HO$.
Mercaptan = Hydrosulphuret of sulphuret of ethule = $AeS + HS$.

As water, in the hydrates of bases, for example,—in alcohol,—acts the part of a weak acid, so does the sulphuretted hydrogen (hydrosulphuric acid) in mercaptan; and, in many compounds derived from it, the hydrogen of the sulphuretted hydrogen is replaced by a metal, producing a metallic sulphuret, which combines with the sulphuret of ethule. This happens when metallic oxides are placed in contact with mercaptan, when the hydrogen of the sulphuretted hydrogen and the metal of the oxide exchange places.

$$(AeS + HS) + MO = (AeS + MS) + HO.$$

Where the metal forms with sulphur a highly negative sulphuret, the resulting compound with the positive or basic sulphuret of ethule is permanent and not easily decomposed; as in the cases of lead, copper, silver, gold, and mercury. But where the resulting sulphuret is more positive or basic, its affinity with the sulphuret of ethule is weak, and the compound is unstable, as in the case of potassium or sodium. Hence the hydrates of potash and soda hardly act perceptibly on mercaptan, while the oxides of gold and mercury are acted on by that substance energetically, with disengagement of heat, and formation of stable, well-defined, crystalline compounds. Most of these are decomposed by sulphuretted hydrogen, which, being the strongest sulphur acid, expels the metallic sulphuret, taking its place, and reproducing mercaptan.

In the production of mercaptan, the sulphate of oxide of ethule and of lime acts on the hydrosulphuret of sulphuret of potassium, producing sulphate of potash, sulphate of lime, and hydrosulphuret of sulphuret of ethule, as in this scheme:—

Sulphuretted hydrogen, Sulphuret of potassium, and Sulphate of oxide of ethule & lime

$$HS + KS \qquad 2SO_3 + AeO + CaO$$

give

Sulphuretted hydrogen, Sulphuret of ethule, and Sulphates of potash and lime.

$$HS + AeS \qquad 2SO_3 + KO + CaO$$

COMPOUNDS OF SULPHURET OF ETHULE.

These compounds are commonly produced by the direct action of the aqueous or alcoholic solution of mercaptan on the metallic oxides, chlorides, or salts. The nature of the reaction has been already explained. In the case of potassium and sodium, the compounds can only be formed by the action of these metals on mercaptan; in this case hydrogen gas is evolved, and white crystalline compounds of sulphuret of ethule with the sulphurets of potassium and sodium are produced. These compounds are instantly decomposed by water, producing potash or soda, and reproducing mercaptan.

The compounds of sulphuret of ethule with the sulphurets of lead, copper, mercury, and gold, resist the action of alkalies, and of most acids: they are insoluble in water.

Sulphuret of Lead and Ethule. Mercaptide of Lead.—Formula, $AeS + PbS$. Lemon-yellow needles and scales.

Sulphuret of Mercury and Ethule. Mercaptide of Mercury.—Formula, $AeS + HgS$. It forms a white crystalline pearly mass, unctuous to the touch, fusible at 188°, soluble in boiling alcohol, from which it crystallizes on cooling. By a strong heat it is decomposed; producing cinnabar, metallic mercury, and a colourless volatile liquid, not yet examined.

Sulphuret of Gold and Ethule. Mercaptide of Gold.—Forms a colourless, thick, gelatinous precipitate. When distilled it yields a colourless liquid, not examined, depositing a little sulphur and metallic gold.

BISULPHURET OF ETHULE.

Discovered by Morin. This compound is obtained when two parts of sulphuret of potassium and three parts of the double sulphate of ethule and potash are subjected to distillation with their equal weight of water. The ethereal liquid which is the product of the distillation is a mixture of several compounds, one of which is the bisulphuret of ethule. It boils at 304° F., is colourless, and of an extremely disagreeable smell. Its formula is $C_4H_5S_2{=}AeS_2$. The mixture obtained by the distillation has received the name of Thialic oil.

SULPHOETHULIC ACID.

When mercaptan is heated gently with nitric acid, 1 eq. of hydrogen is oxidized, and a new acid is formed, discovered by Löwig, which contains the elements of sulphuric acid and of sulphuret of ethule, $AeS + SO_3 = C_4H_5S_2O_3$. It forms with bases easily crystallizable salts, which are very soluble in water. During its formation, a certain quantity of mercaptan is entirely decomposed, and sulphuric acid produced, but this can be separated by saturating the liquid with baryta, which forms a soluble salt with sulphoethulic acid.

SELENIURET OF ETHULE

Is obtained, according to Löwig, by distilling seleniuret of potassium with sulphovinate of lime or potash.

Probable formula, $AeSe$, or $AeSe + HSe$.

CYANIDE OF ETHULE.

Discovered by Pelouze. A dry mixture of equal parts of sulphovinate of potash and cyanide of potassium is subjected to distillation, and the product rectified along with chloride of calcium. It is a colourless liquid of a penetrating garlic odour, boiling at 180°. Sp. g. 0·700. Is decomposed by oxide of mercury, but not by the alkalies. It is highly poisonous, inflammable, miscible with alcohol and ether, sparingly dissolved by water. In its production, the oxide of ethule in the sulphovinate, acting on the cyanide of potassium, produces potash, which unites with the sulphuric acid, and cyanide of ethule, which distils over.

Formula, $AeCy$.

SULPHOCYANIDE OF ETHULE.

By distilling sulphocyanide of potassium with a mixture of sulphuric acid and alcohol, a heavy oily liquid is obtained, of a most offensive smell, while the residue contains sulphates of potash and ammonia. The liquid seems to contain no nitrogen, and if so, cannot be a sulphocyanide of ethule. It is sometimes called sulphocyanic ether; but its nature is not yet known.

SALTS OF OXIDE OF ETHULE.

Oxide of ethule (ether) forms with acids neutral and acid salts. In regard to its power of neutralizing acids, it follows the general laws of the capacity of saturation of the acids. The neutral salts of oxide of ethule have no action on vegetable blues. They differ from inorganic salts in this, that the acid or the oxide of ethule are not replaced by other acids or metallic oxides, when their solutions are mixed with those of inorganic salts, at the ordinary temperature. For example, oxalate of oxide of ethule (oxalic ether) gives no precipitate of oxalate of lime with an alcoholic solution of chloride of calcium.

In contact with hydrated alkalies, they are decomposed; slowly at the ordinary temperature, rapidly if boiled. The alkali combines with the acid, while the oxide of ethule and the hydratic water of the alkali combine in the nascent state, producing alcohol.

Many of these neutral salts are only half decomposed by alkalies and metallic oxides, so that double salts of oxide of ethule and metallic oxides are formed. All such double salts hitherto known are soluble in water; and possess, in reference to the state of the oxide of ethule contained in them, the same character as the neutral salts; so that the acids they contain cannot be precipitated by the usual reagents. In this they are analogous to the double salts which sesquioxide of cromium and some other bases form with oxalic acid, in which the oxalic acid cannot be detected by a salt of lime. The metallic oxide in these double salts of oxide of ethule may be replaced by other metallic oxides, or removed by a stronger acid. In the latter case it is replaced by water, and the acid salts of oxide of ethule (for example, sulphovinic, phosphovinic, or oxalovinic acids, as they are called) are produced.

These acid salts of ethule possess, in the concentrated state, considerable stability, and may be heated to 212° without decomposition. Many of them, the acids of which form hydrates which are not volatile, are resolved by heat into ether, which distils off, and the acid, or rather its hydrate, which remains behind. If these acid salts of ethule be much diluted, they are decomposed at the ordinary temperature, and still more rapidly if boiled; a hydrate of the acid is formed, and the oxide of ethule combines with water, producing alcohol.

If a concentrated solution of the acid sulphate of oxide of ethule be heated with the hydrates of many other acids, it most commonly happens that these other acids unite with the oxide of ethule to form neutral salts, while a hydrate of sulphuric acid is left. Thus mucic acid, oleic acid, stearic acid, &c. when heated with a mixture of sulphuric acid and alcohol, yield the mucate, oleate, and stearate of oxide of ethule, &c.

When the concentrated acid salts of oxide of ethule are distilled along with other salts, the acids of which are volatile, and form volatile compounds with oxide of ethule, the acid of the acid salt of oxide of ethule combines with the base of the other salt, and the oxide of ethule distils over in combination with the volatile acid. In this way are the neutral salts of oxide of ethule with all volatile acids prepared. Example: acid sulphate of oxide of ethule (sulphovinic acid) distilled with acetate or formiate of potash, gives neutral acetate or formiate of oxide of ethule, and bisulphate of potash.

The neutral double salts of oxide of ethule, heated or distilled with many acids, are decomposed into an acid salt of a metallic base which remains behind, while the oxide of ethule combines with the acid which was added. Example: sulphate of potash and oxide of ethule (sulphovinate of potash), heated with hydrated acetic or œnanthic acid, yields acetate or œnanthate of oxide of ethule, while bisulphate of potash is left.

Chloride of benzule, heated with alcohol, is resolved, at the expense of the water of the alcohol, into hydrochloric acid and benzoic acid. The latter combines, in the nascent state, with the oxide of ethule, forming benzoate of oxide of ethule (benzoic ether), which distils over.

OXIDE OF ETHULE AND SULPHURIC ACID.

The neutral sulphate of oxide of ethule is unknown. The acid sulphate, known under the names of sulphovinic and ethereo-sulphuric acid, is obtained directly by bringing the vapour of ether into hydrated sulphuric acid, as long as it is absorbed. Water being added to the mixture after some hours, the uncombined ether is separated, but a great part remains combined with the sulphuric acid. It is, however, prepared most easily, and in largest quantity, by heating a mixture of hydrated sulphuric acid and alcohol.

The acid decomposes the alcohol, uniting with the ether; while the water, both of the alcohol and of the acid, combines with the acid sulphate of oxide of ethule.

[As ether is obtained by distilling such a mixture, the effect of heat on it has been the subject of many laborious investigations, which have led at different times to conflicting theories on the formation of ether. In the following pages will be found a collection of all the established facts connected with this very interesting subject, together with that view of the production of ether which appears most consistent with those facts. We are indebted for it to Liebig, whose researches on this subject have powerfully contributed to dissipate the obscurity in which it was so long enveloped. —Editor.]

a. It has been observed that hydrated sulphuric acid, containing as much as 55 p. c. of water (1 at. anhydrous acid and 4 at. water), does not decompose alcohol at the ordinary temperature, but that at the boiling temperature it does so, producing the acid sulphate of oxide of ethule.

b. It has further been proved, that, by cooling this mixture, the proportion of acid sulphate of ethule again diminishes, and that by diluting it with water the acid sulphate undergoes a further decomposition.

c. In this case the oxide of ethule separates from the acid, and unites with water, reproducing alcohol.

d. A mixture of 9 parts of oil of vitriol ($So_3 + HO$) with 5 parts of alcohol at 85 per cent., after having been heated to its boiling point, contains exactly the elements of 2 at. anhydrous acid and 1 at. ether, or 1 at. anhydrous bisulphate of oxide of ethule, and 4 at. water.

According to the common opinion, the 2 at. of sulphuric acid act on 1 at. alcohol, so that only half of the acid combines with ether; thus producing, on the one hand, anhydrous bisulphate of ethule, and on the other a diluted hydrated acid with 4 atoms of water, while one-half of the alcohol remains uncombined in the solution. Both suppositions are totally without foundation.

e. It is obvious that, if the bisulphate of oxide of ethule has a composition analogous to that of the double salts of that base, it must contain, along with the oxide of ethule, a certain quantity of water replacing the metallic oxide in the double salt. There is besides reason to believe, from the phenomena of the distillation of ether, that the bisulphate of oxide of ethule has as strong an affinity for water as the sulphuric acid which it contains. But in this case the mixture must contain an acid with less than 4 atoms of water; which, as we have seen (*a*), cannot exist along with free alcohol, without decomposing it, and producing bisulphate of oxide of ethule.

f. A mixture of 100 parts oil of vitriol, 48 parts alcohol, and 18½ parts water, (2 at. sulphuric acid, 1 at. ether, and 6 at. water,) boils at 284°. Now if only half the sulphuric acid is present in the state of bisulphate of oxide of ethule (anhydrous), then there must also be present along with the free alcohol, a hydrated acid with 6 at. water. But acid of this strength boils at 222°.

g. When dry chlorine gas is passed through both the mixtures above-mentioned, no hydrochloric acid is formed. Now since free alcohol boils at 173°, and is instantly decomposed by chlorine, with the production of hydrochloric acid, and other compounds containing chlorine, while the salts of oxide of ethule, on the contrary, are not altered by chlorine, the above facts show that the mixture contains no free alcohol. Further, since the oxide of ethule and sulphuric acid in the mixture are present in the proportions in which they exist in the bisulphate of oxide of ethule, it follows that the mixture can contain no free acid, and must therefore be considered as a compound of bisulphate of oxide of ethule with water.

h. When the mixture is heated beyond 284°, the bisulphate of oxide of ethule is decomposed into ether and water, which distil over. An effervescence, similar to brisk ebullition, takes place, because the ether at that temperature assumes the form of gas. If oil of vitriol be added, the temperature must be raised to form 300° to 330° before this decomposition occurs; and with a great excess of sulphuric acid the mixture blackens, yielding only traces of ether, while the greater part of it is resolved into new products.

i. If alcohol be added to the original mixture, the alcohol passes over anhydrous, till the temperature rises to 258° or 260°, when traces of ether appear. At this temperature, therefore, the decomposition of the bisulphate of oxide of ethule begins, when an excess of alcohol is present. If so much water is added as to keep its boiling point below 258°, alcohol alone, without ether, distils over.

k. If a current of dry air be made to pass through the mixture while heated to 284°, the boiling point sinks to 270°, and this reduction of temperature causes the production of ether to cease, alcohol alone passing over.

All these phenomena are explained by the following considerations:—

l. At temperatures above 284°, the bisulphate of oxide of ethule is decomposed into ether which separates as gas, and sulphuric acid which mixes with the undecomposed portion.

m. If we consider each particle of the bisulphate of oxide of ethule as composed of ether, anhydrous sulphuric acid, and water, it is clear that the anhydrous acid, at the moment of its separation from the ether, must seize on all water, free or combined, in the vicinity of the ether.

n. Thus, at the moment the ether becomes free, the anhydrous acid, also set free, prevents it from uniting with water to form alcohol. But when the gaseous ether passes through the undecomposed hydrated bisulphate of oxide of ethule, a certain proportion of the water of that compound must evaporate in the dry gas, and in these circumstances the ether and water do not combine together.

The surface of the effervescing liquid has the temperature at which bisulphate of oxide of ethule is decomposed, but at this temperature, 284°, the water of that compound is gaseous. There are thus produced, simultaneously, water in the gaseous form by evaporation, and ether, also gaseous, by decomposition; which, as both are in the nascent state, unite to form alcohol.

Thus the alcohol, always observed to distil over with the ether, is derived from the surface; the ether and water which distil over proceed from the decomposition in the interior of the liquid. This explains why no ether is obtained when the liquid is not in brisk ebullition, no matter how high the temperature may be; it explains further, why more alcohol is obtained when a current of dry air passes through the liquid, since in that case the same decomposition goes on in the interior of the liquid as generally occurs at the surface.

In proportion as the quantity of water in the bisulphate of oxide of ethule is increased, the tension, that is, the quantity of water evaporating at a given temperature, increases also. A solution of the bisulphate containing 4 atoms of water, must give off at 284° less water than one containing 5 or 6 atoms of water. This consideration explains the following phenomena:—

When the above-mentioned mixture, consisting of 2 at. anhydrous acid, 1 at. ether, and 4 at. water, is distilled, ether, alcohol, and water pass over at 284°; and the first portion contains 19 of water to 100 of ether. Its sp. g. is 0·758. There has, therefore, distilled less water than the proportion necessary to form alcohol with the ether, namely, 22·36 of water to 100 of ether. If the mixture distilled contain 2 at. anhydrous acid, 1 at. ether, and 5 at. water = 100 parts acid, 48 alcohol, and 18½ water, the product of the distillation has the sp. g. 0·778, and contains 21·43 of water to 100 of ether. With a mixture of 2 at. acid, 1 at. ether, and 6 at. water = 100 parts acid, 48 alcohol, and 27 water, the product contains 22 of water to 100 of ether, and has the sp. g. 0·796 to 0·798. But this is, as nearly as possible, the sp. g. of alcohol. When, therefore, in this mixture, there are 3 atoms of water for 1 of acid, the gaseous ether carries off its own volume of the vapour of water.

If we imagine, in this last mixture, one half of the bisulphate of oxide of ethule decomposed, it will then contain

$$\left.\begin{array}{l}1 \text{ at. dry acid} \\ \frac{1}{2} \text{ at. ether}\end{array}\right\} \text{combined as bisulphate of ethule,}$$

1 at. free acid,
5½ at. water.

If we now add ½ at. alcohol, the free acid will decompose this alcohol, and we shall have the original mixture of 2 at. dry acid, 1 at. ether, and 6 at. water. This mixture yields ether and water in the proportions to form alcohol. It is obvious that the proportions are in no way altered if alcohol is merely added in volume exactly equal to the liquid distilled off, which contains the elements of alcohol. In this case the acid retains its power to cause alcohol to be resolved into ether and water, to infinity. But in preparing ether, pure alcohol is not used, only spirit of from 85 to 90 per cent.; so that with every drop of alcohol which is added, there is introduced more water than corresponds to the above proportion (1 at. acid to 3 water).

Now it has been mentioned that sulphuric acid, combined with 4 at. water, is still capable, with the aid of heat, of converting alcohol into bisulphate of oxide of ethule. In this case, 2 at. acid take up 1 at. ether, and the resulting bisulphate contains 9 at. water, namely, 8 from the acid, and 1 from the ether. But such a mixture, which boils at 258°, produces alcohol alone, not ether.

An acid containing 4½ at. water boils alone at 258°, namely, at the point where the decomposition of the bisulphate of ethule begins. It is therefore clear, that when this diluted acid, combined with ether, is made to boil, water is produced simultaneously with ether at all points where the latter is formed. But when water and ether meet in the nascent state, they unite to form alcohol. Hence the proportion of 9 at. water to 2 of dry acid, is the limit of the dilution of the bisulphate, beyond which boiling produces no ether. When ether, therefore, is prepared from alcohol which is not anhydrous, we shall obtain ether, until, by the addition of the water introduced with the alcohol, a mixture is formed containing 4½ at. water to 1 at. dry acid.

Experience has shown that when a mixture of 9 parts oil of vitriol and 5 parts alcohol at 90 p. c. is employed, the production of ether ceases when 31 parts of such alcohol have been added. If more be added, alcohol alone distils over, with a mere trace of ether.

Supposing the whole water of this spirit to remain behind, while the elements of pure alcohol, in the form of ether and water, distil over, the residue contains at this point rather more than 3 at. water to 1 at. dry acid. But since, in the beginning of the distillation, more ether, or less water, passed over, than the proportion necessary to produce alcohol, we may consider, without risk of error, 3½ to 4 at. water to 1 at. dry acid as the limit fixed by experience for the productive preparation of ether. From this point, when alcohol not anhydrous is added, as the liquids cannot instantly mix, there is produced, at some points, a mixture containing 4½ at. water to 1 at. dry acid; which, as above shown, yields no ether when boiled.

The addition of an excess of sulphuric acid to the mixture prevents the decomposition of the bisulphate of oxide of ethule, till the temperature rises so high that new reactions take place between the elements of the oxide of ethule and the sulphuric acid. This happens at about 320°. The principal products of this reaction are, sulphurous acid, olefiant gas, water, and carbon. In certain proportions acetic acid is formed. With a great excess of acid, traces of formic acid and carbonic oxide are produced. As long as olefiant gas comes off, carbonic acid cannot be detected. During this decomposition, sulphurous acid and olefiant gas are given off in equal volumes, which sufficiently explains the reaction.

The elements of 1 atom bisulphate of oxide of ethule arrange themselves as follows :—

2 at. sulphurous acid . .	S_2			O_4
2 at. olefiant gas . . .		C_2	H_2	
3 at. water			H_3	O_3
2 at. carbon		C_2		
	S_2	C_4	H_5	O_7

Carbon and water are the elements of acetic acid, the formation of which must diminish the quantity of carbon in the residue. By the action of the sulphuric acid in excess on acetic acid, formic acid and sulphurous acid are formed; and by the action of the sulphuric acid in excess on formic acid, carbonic oxide gas is produced.

It is probable that, in this decomposition, the elements of sulphuric acid and ether first arrange themselves so as to form ethionic or isethionic acids, and that the above-named products are derived from the further decomposition of these acids. At least Ettling found in the residue an acid agreeing in many of its properties with isethionic acid. But the formation of these substances would not alter the proportions of the ultimate products.

The sulphate of oxide of ethule and etherole (sweet oil of wine) is produced in small quantity. This is easily explained, as the composition of that body represents neutral sulphate of ethule — 1 at. of water. The carbon of the residue, when washed and dried, forms a black powder, soiling paper or the finger strongly. If heated, it yields first water, then sulphur. The sulphur it contains cannot be extracted from it by alkalies or sulphuret of carbon.

The purest bisulphate of oxide of ethule is obtained when the sulphate of oxide of ethule and etherole (sweet oil of wine) is gently heated with 4 parts of water. It is decomposed; etherole, in the form of a yellow oil, separating, while bisulphate of oxide of ethule is dissolved by the water. By adding sulphuric acid to a solution of the sulphate of baryta and oxide of ethule till all the baryta is precipitated, or by decomposing the sulphate of lead and oxide of ethule by sulphuretted hydrogen, the bisulphate may also be prepared.

It forms with water a very sour liquid. It cannot be evaporated, when diluted, without decomposition. With bases it forms a series of double salts.

Formula, $AeO,SO_3 + HO,SO_3$.

DOUBLE SALTS OF THE SULPHATE OF OXIDE OF ETHULE.

When the bisulphate of oxide of ethule is neutralized by bases, double salts are formed, containing 2 at. sulphuric acid, 1 at. oxide of ethule, and 1 at. of the base which is added. They are, without exception, soluble in water and hydrous alcohol, whence it happens that the sulphuric acid they contain is not detected by the usual reagents. But if to a solution of one of these double salts hydrochloric acid be added, and the mixture heated to boiling, alcohol is expelled with the vapour of water, and in the residual liquid the sulphuric acid can now be recognized. When exposed to heat they are decomposed, and, according to the temperature they yield sulphate of oxide of ethule and etherole, with alcohol, sulphurous acid, olefiant gas, and in the residue a sulphate mixed with carbon. Distilled with quick lime at a temperature not higher than 300°, they are entirely converted into sulphates and the two first-mentioned products. The double salt of baryta, distilled with a diluted sulphuric acid containing 4 at. water, yields a mixture of ether and alcohol. Most of them contain water of crystallization, which they part with entirely in vacuo over sulphuric acid at the ordinary temperature. The double salt of potash alone crystallizes without water. When boiled in the form of concentrated solution in water, they are decomposed, although slowly. Bisulphates, or mixtures of sulphuric acid and neutral sulphates, are left, while alcohol passes over. Heated in the dry state, with hydrate of baryta or of lime, these salts are resolved into fixed neutral sulphates and alcohol. Chlorine gas, passed through their solutions, does not decompose the oxide of ethule, nor set sulphuric acid free. When supersaturated with potash, the salts of potash and soda may be boiled and evaporated without decomposition. If the dry salts are melted with the hydrated alkalies, the oxide of ethule is destroyed, and all the sulphuric acid remains combined with the alkali.

To prepare these salts, a boiling hot mixture of equal parts of oil of vitriol and alcohol of 85 p. c. is saturated with milk of lime, carbonate of baryta or carbonate of lead, when a soluble double sulphate of oxide of ethule with lime, baryta, or oxide of lead, is formed, and separated by filtration from the insoluble sulphates of those bases. If one of these salts be mixed with carbonate of potash, soda, or ammonia, the insoluble carbonate is precipitated, and the filtered liquid contains the double salt of oxide of ethule with the alkaline base. Or the free bisulphate of oxide of ethule is saturated with a base; or lastly, the double salt of baryta is precipitated by a soluble sulphate. In this last way are prepared the double salts of oxide of ethule with magnesia, oxide of manganese, &c. As the other properties of these salts offer no peculiar interest, it is unnecessary to detail them.

General formula for these double salts, $AeO,SO_3 + MO,SO_3 +$ aq. They are often described under the name of sulphovinates or ethereosulphates.

Sulphate of Oxide of Ethule and Potash.—Formula, $AeO,SO_3 + KO,SO_3$ (Marchand). Forms transparent and colourless scales, like chlorate of potash, permanent in the air, soluble in its own weight of water, of a sweetish saline taste, soluble in spirit of wine, insoluble in absolute alcohol and ether. When heated beyond 212°, it is decomposed without undergoing fusion.

Sulphate of Oxide of Ethule and Baryta.—Formula, $AeO, SO_3 + BaO,SO_3 + 2$ aq. (Marchand). Brilliant transparent tables, permanent in the air, or rhombic prisms, of a sharp saline taste, soluble in their own weight of water, insoluble in cold, sparingly soluble in hot anhydrous alcohol. It loses half of its water by boiling with alcohol, and the whole of it in a current of air at 112°, or in vacuo at the ordinary temperature. The hydrous salt is decomposed at 212°, the anhydrous is not.

Sulphate of Oxide of Ethule and Lime.—Formula, $AeO,SO_3 + CaO,SO_3 + 2$ aq. (Serullas, Marchand). Large, thin, six-sided plates; 4 parts of water at 65° dissolve 5 parts of salt. It is soluble in absolute alcohol with the aid of heat. When distilled, it yields besides the usual products, according to Marchand, a peculiar volatile liquid, in very minute quantity, which is miscible with water, alcohol, and ether.

Sulphate of Oxides of Ethule and Lead.—1. Neutral. Formula, $AeO,SO_3 + PbO,SO_3 + 2$ aq. (Dumas, Marchand). Large colourless transparent tables, very soluble in water and alcohol, reddening litmus. Gradually undergoes spontaneous decomposition, exhales ether, and becomes unctuous from sulphate of oxide of ethule and etherole.—2. Basic. Formula, $AeO,2PbO,2SO_3$. Formed by digesting the neutral salt with oxide of lead. It is an uncrystallized white mass, very soluble in water and alcohol, not changing vegetable blues. It yields, when distilled, alcohol and sulphate of oxide of ethule and etherole, without any other volatile products.

OXIDE OF ETHULE AND PHOSPHORIC ACID.

Acid Phosphate of Oxide of Ethule. Syn. Phosphovinic Acid; Ethereophosphoric Acid. — When hydrated phosphoric acid, $P_2O_5 + 3HO$, is mixed with alcohol, much heat is developed. Of the three atoms of basic water which the acid contains, one is replaced by oxide of ethule, producing an acid salt with 3 atoms of base, analogous to the common phosphates. If the acid be diluted with so much water as to have the sp. g. 1·2, it no longer decomposes alcohol. (Pelouze.)

It is obtained pure by decomposing the phosphate of baryta and oxide of ethule by sulphuric acid: 100 parts of the crystallized salt require 25·33 sulphuric acid (oil of vitriol). The sulphate of baryta being separated by the filter, the solution is evaporated, first in the water-bath, afterwards in vacuo over sulphuric acid. (Pelouze.)

It forms a syrupy, colourless, very acid liquid, miscible with water, alcohol, and ether. It may be boiled in the diluted state without decomposition. The concentrated acid at a high temperature is decomposed, with disengagement of ether, alcohol, and inflammable gases, and deposition of carbon. It coagulates albumen. In the most concentrated state it shows a tendency to crystallize. Formula, $P_2O_5 + AeO + 2HO$.

PHOSPHATE OF OXIDE OF ETHULE WITH METALLIC OXIDES.

If the acid phosphate of oxide of ethule be brought in contact with metallic oxides, the two atoms of basic water contained in it are separated, and replaced by their equivalent of metallic oxide; and salts with 3 atoms of base are formed, according to the general formula, $P_2O_5 + \left.\begin{matrix} AeO \\ 2MO \end{matrix}\right\}$. MO here is a metallic protoxide. Compounds of pyrophosphoric or metaphosphoric acids with oxides of ethule have not yet been formed.

The phosphates of oxide of ethule and other bases may be formed either by neutralizing the acid phosphate directly by the metallic oxide, or by precipitating the phosphate of oxide of ethule and baryta with soluble carbonates or sulphates.

Phosphate of Oxide of Ethule and Baryta. Syn. Phosphovinate or Ethereophosphate of Baryta.—Formula, $P_2O_5 + 2BaO + AeO + 12$ aq. Phosphoric acid, evaporated to the consistence of thick syrup, is mixed with its own weight of pure alcohol or spirit of wine at 92 p. c. the mixture heated to the boiling point, and, after twenty-four hours, diluted with water, and neutralized with carbonate of baryta at the ordinary temperature. The solution is filtered from the precipitated phosphate of baryta, and evaporated at 100° till it crystallizes. It forms colourless, pearly, six-sided tables, soluble in 11 parts of water at 100°, in 15 parts at 68°, in 30 parts at 32°, and in 36 parts at 212°. A solution saturated at 100°, becomes thick when heated to the boiling point, from the deposition of the hydrous salt. The water amounts to 29·1 p. c. At 302° it is entirely expelled. (Pelouze.)

OXIDE OF ETHULE AND ARSENIC ACID.

According to D'Arcet, concentrated arsenic acid, when heated with alcohol, forms an acid salt, differing in its constitution from the acid phosphate. The acid arseniate of oxide of ethule contains 3 atoms of base, namely 2 at. oxide of ethule and 1 at. water, which last may be replaced by metallic oxides. Its formula is $As_2O_5,2AeO,HO$; and the general formula for its double salts is $As_2O_5,2AeO,MO$. These statements require confirmation.

OXIDE OF ETHULE AND NITRIC ACID.

Nitric acid decomposes ether, without combining with it. A mixture of alcohol and strong nitric acid at the ordinary temperature spontaneously boils. Many different products are formed, according to the strength of the acid and the temperature. With a dilute acid, or if the reaction be moderated by cold, two only are produced; namely, aldehyde and nitrite (hyponitrite) of oxide of ethule. When the acid is concentrated, besides these there are formed products of the oxidation of carbon, carbonic and oxalic acids, also acetic and formic acids, besides acetate and formiate of oxide of ethule.

OXIDE OF ETHULE AND HYPONITROUS ACID.

Hyponitrite of Oxide of Ethule. Syn. Nitrous Ether; Hyponitrous Ether.—To prepare this compound in a state of purity, the following process has lately been given by Liebig. One part of starch, and 10 parts of nitric acid, sp. g. 1·3, are introduced into a capacious retort, which is connected by means of a wide tube, bent at right angles, with a two-necked bottle, so that the further end of the tube reaches to the bottom of the bottle. Into this bottle is introduced a mixture of 2 parts of alcohol at 85 p. c. and 1 part of water, and it is surrounded by cold water. The second aperture of the bottle is connected, by means of a long and wide tube, with a good cooling apparatus or condenser. The starch and nitric acid are heated in the water-bath; pure hyponitrous acid is disengaged, which, passing through the alcohol, instantly combines with the ether, forming hyponitrite of oxide of ethule, which distils in a continuous stream. This process is very productive. By means of water, the new ether is purified from alcohol, and by standing over chloride of calcium it is freed from water. The tube which connects the retort with the two-necked bottle must have a length of 2 or 3 feet, and must be surrounded with moist paper during the operation. If the alcohol be not carefully cooled, it becomes spontaneously hot and boils violently. From this moment the hyponitrite of ethule is no longer pure.

The following methods, which are commonly given, yield a product contaminated by aldehyde in variable quantity. 2. Two parts of alcohol of 85 p. c. are mixed with 2 parts of nitric acid of sp. g. 1·284, and the mixture is gently heated in a retort connected with a condenser surrounded with ice. The mixture quickly boils, and the fire is instantly removed. When no more passes over, the ethereal compound is purified by rectification at a very gentle heat. 3. In a strong cylindrical vessel are placed 9 parts of alcohol at 85 p. c. By means of a funnel tube ending in a narrow aperture, 4 parts of water are introduced below the alcohol, taking care that they do not mix. In the same manner 8 parts of fuming nitric acid are added under the water, so that the bottle contains three strata of liquid. It must be filled to four-fifths; and in order that the stratum of water may be deep enough, the bottle should be three times as high as it is wide. It is now lightly stopped, and left to itself in a temperature not higher than 53°. After two or three days, there are found in the bottle two strata, the uppermost of which is the ether, to be purified by rectification.

The hyponitrite of oxide of ethule prepared by process 1 is pale yellow, has a most fragrant smell of apples and Hungary wines, boils at 62°, and has the sp. g. 0·947 at 60°. It may be mixed with an alcoholic solution of potash without becoming brown; hyponitrite of potash and alcohol are formed. That made by processes 2 and 3 boils at 70°, has the sp. g. 0·886 at 40°. Its smell is like that of the former, but at the same time suffocating. Mixed with an alcoholic solution of potash, it becomes dark brown, with production of resin of aldehyde. It is highly combustible, burning with a white flame. The ether of processes 2 and 3, when kept, becomes acid, while nitric oxide gas is given off. Hence it often bursts the bottles. It must, therefore, and on account of its great volatility, be kept in half-ounce or ounce bottles very strongly made, in a cool place. This tendency to become acid is greater when air is admitted, and depends on the presence of aldehyde, which is oxidized by the oxygen of the air, or of the hyponitrous acid. If the liquid is allowed to remain in contact with milk of lime or aqua potassæ, the aldehyde is converted into resin of aldehyde; and the liquid is found to contain nitrate and hyponitrite of lime, with another salt of lime, not examined. By allowing the hyponitrite of oxide of ethule to stand over dry nitrate of lime, and rectifying it along with that salt, it is rendered pure from alcohol and water. It is soluble in 48 parts of water, and miscible in all proportions with ether and alcohol.

Formula, AeO,NO_3.

The spiritus ætheris nitrosi, or sweet spirit of nitre of the pharmacopœia, is a mixture of nitrous ether (the impure hyponitrite of oxide of ethule above described) with rectified spirit of wine. It may be made by directly mixing these liquids, or by distilling nitric acid with a much larger proportion of alcohol than in the preceding processes. For example, 1 part of diluted nitric acid may be distilled with 6 parts of alcohol at 85 or 90 p. c., and 5 parts of distilled product drawn off. Its properties for the most part coincide with those of nitrous ether, but its sp. g. is 0·825. It ought to be neutral; but must be carefully preserved in small bottles, from the contact of air, as it otherwise gradually becomes acid. It is employed as a refrigerant and diuretic.

OXIDE OF ETHULE WITH CARBONIC ACID.

The only compound under this head which has yet been obtained directly, is the double carbonate of oxide of ethule and potash. But the neutral carbonate of oxide of ethule (carbonic ether) has been formed indirectly by the action of potassium or sodium on neutral oxalate of oxide of ethule (oxalic ether); a reaction which has not yet been fully explained.

Carbonate of Oxide of Ethule and Potash. Syn. Carbovinate of Potash.—Formula, $AeO,CO_2 + KO,CO_2$. Discovered by Dumas and Peligot. Hydrate of potash, fused at a red heat, is dissolved in alcohol, and the solution is saturated with dry carbonic acid gas. The liquid congeals to a white paste, which contains the new double salt along with neutral carbonate and bicarbonate of potash. The mass is placed on a filter, and washed with pure ether; it is then covered with absolute alcohol, which dissolves the double salt alone. This solution, when mixed with ether, deposits the salt in crystals, which are collected on a filter, carefully pressed in bibulous paper, and dried in vacuo over sulphuric acid.

It forms pearly soft scales, unctuous to the touch, which, when distilled, yield carbonic acid, an ethereal liquid, an inflammable gas, and a residue composed of carbon and carbonate of potash. When placed in contact with water, this salt is instantly resolved into alcohol and bicarbonate of potash.

With ammonia and alcohol, carbonic acid forms a similar salt, which, however, cannot be separated in the same way from the carbonates of ammonia formed along with it.

CARBONATE OF OXIDE OF ETHULE.

Syn. Carbonic Ether. — Formula, AeO,CO_2. Discovered by Ettling. Fragments of potassium or sodium are gradually added to warm oxalic ether (see below), as long as gas is disengaged. The excess of metal being removed, the semi-solid mass produced is mixed with water and distilled, when the carbonic ether swims on the surface of the product of the distillation. Having separated it from the water, it is dried by contact with chloride of calcium, and rectified with potassium or sodium, till a portion, when acted on by caustic potash, yields no oxalate of potash. It forms a colourless, very fluid, ethereal liquid, possessing a burning taste and an aromatic ethereal odour, resembling that of oxalic ether. It is lighter than water, has the sp. g. 0·975 at 66°, boils at 260°, is kindled with difficulty and burns with a blue flame. It may be mixed with alcohol and ether, but is insoluble in water. When mixed with an alcoholic solution of hydrates of potash or soda, it is quickly resolved into alcohol, and carbonate of potash or soda, which separate either as an oily concentrated solution in water, or as a crystalline powder if no water be present. The formation of carbonic ether, which is attended by the production of several substances not yet examined, is as yet unexplained. According to Löwig's experiments, when sodium is made to act on oxalic ether, a suboxide of carbon, C_2O, and carbonic ether are produced.

$$\left.\begin{array}{lll}\text{2 at. carbonic ether} & =C_{10}H_{10}O_6 & \\ \text{1 at. soda} & = \phantom{C_{10}H_{10}}O & Na \\ \text{1. at. suboxide of carb.} & =C_2\phantom{H_{10}}O & \end{array}\right\}=\left\{\begin{array}{lll}\text{2 at. oxalic ether} & =C_{12}H_{10}O_8 & \\ \text{1 at. sodium} & = & Na \\ & & \end{array}\right.$$

$$C_{12}H_{10}O_8,Na \quad = \qquad\qquad = C_{12}H_{10}O_8,Na.$$

A part of the carbonic ether is decomposed by sodium into carbonic oxide and soda-ether, AeO,NaO. When soda-ether comes in contact with water, alcohol and hydrate of the alkali are produced. The compound of the suboxide of carbon and soda is decomposed by water into formiate and nigrinate of soda. According to Löwig, nigrinic acid, $C_{14}H_7O_7$, is produced by the decomposition of oxalic ether by sodium. It has a brownish red colour and a resinous appearance. It is formed by the suboxide of carbon, combining with the elements of water; $14(C_2O) + 8NaO + 14HO = 7(C_2HO_3,NaO) + C_{14}H_7,O_7,NaO$.

OXIDE OF ETHULE AND OXALIC ACID.

Oxalic acid forms with oxide of ethule an acid salt and a neutral salt. The analysis of the latter by Dumas and Boullay first gave correct notions in regard to the composition of the so-called compound acid ethers.

Neutral Oxalate of Oxide of Ethule.—Syn. Oxalic Ether.—Discovered by Thenard. Formula, $AeO,\bar{O}x$. To prepare it, 4 parts of binoxalate of potash are mixed in a retort with 5 parts of oil of vitriol and 4 of alcohol at 90 p. c.; and distilled with a quick fire. As soon as the product is rendered turbid by the addition of water, the receiver is changed, and is no longer kept cool. The subsequent product is quickly mixed with 4 times its bulk of water, the ether which sinks to the bottom is separated, and agitated 4 or 5 times with new portions of water till it becomes neutral to test paper. The ether thus washed is introduced into a small dry retort, which must be filled up to nine-tenths of its capacity, and rectified. As soon as the product becomes clear, and the boiling goes on, not by jerks but smoothly, the receiver is changed. What now passes over is pure anhydrous oxalate of oxide of ethule (oxalic ether).—(Ettling.)

It is a colourless, transparent, oily fluid, of sp. g. 1·0929 at 46°, boiling at 370°, miscible with alcohol and ether, and having a peculiar aromatic smell. In a state of purity it may be kept many days under water, in which it is very sparingly soluble without decomposition; but when it contains but a trace of free acid or of alcohol, it is speedily resolved into oxalic acid, which is deposited in large transparent four-sided prisms, and alcohol. The same change occurs with an excess of fixed alkali.

DOUBLE SALTS OF OXALIC ACID WITH OXIDE OF ETHULE AND METALLIC OXIDES.

When oxalic ether is dissolved in alcohol, and so much of a solution of fused potash or soda in alcohol is added as to neutralize one half of the oxalic acid, half of the oxide of ethule separates, and combines with the water of the alkali to form alcohol. It is replaced by the alkali, and double salts are produced, containing 2 at. oxalic acid, 1 at. oxide of ethule, and 1 at. potash or soda. When ammonia is added to oxalic ether, it is decomposed: with an excess of ammonia oxamide is produced: with less ammonia oxamethane is formed. Potassium and sodium decompose oxalic ether, producing carbonic ether and other products.

Binoxalate of Oxide of Ethule. Syn. Oxalovinic Acid.—Formula, $\mathrm{AeO},\bar{\mathrm{O}}\mathrm{x}+\mathrm{HO},\bar{\mathrm{O}}\mathrm{x}$. Oxalate of ethule and potash (see below) is dissolved in alcohol, and fluosilicic acid is added as long as it causes a precipitate. The filtered liquid contains the oxalovinic acid mixed with alcohol and water. It may be obtained free from alcohol by carefully adding sulphuric acid to the aqueous solution of the oxalate of ethule and baryta (oxalovinate of baryta, see below). It forms a very sour liquid, which is easily resolved, especially with the aid of heat, into oxalic acid and alcohol.

Oxalate of Oxide of Ethule and Potash. Syn. Oxalovinate of Potash.—Formula, $\mathrm{AeO},\bar{\mathrm{O}}\mathrm{x}+\mathrm{KO},\bar{\mathrm{O}}\mathrm{x}$. One volume of oxalic ether is dissolved in 2 vol. alcohol, and after trying with a portion of this mixture how much of an alcoholic solution of potash is required to produce a slight alkaline reaction, rather less than half that proportion is added to the remaining mixture. If, for example, 10 fluid drachms of the mixture require 16 fluid drachms of an alcoholic solution of potash to neutralize the acid completely, producing a slight alkaline reaction; then to 100 volumes of the mixture, 75 volumes of the alcoholic solution should be added. The double salt, being insoluble in alcohol, separates. It is washed with alcohol, and dried in vacuo. It forms crystalline scales, anhydrous, and perfectly soluble in alcohol of 75 p. c. It is easily decomposed by acids and alkalies, but when dry it bears a heat of 212° without change.

Oxalate of Oxide of Ethule and Baryta. Syn. Oxalovinate of Baryta.—Formula, $\mathrm{AeO},\bar{\mathrm{O}}\mathrm{x}+\mathrm{BaO},\mathrm{Ox}$. When the oxalovinic acid is neutralized by carbonate of baryta, the liquid evaporated at the ordinary temperature, or in vacuo, yields this double salt. It crystallizes with difficulty, and is extremely soluble in water. By the addition of soluble sulphates to its solution, the corresponding double salts of other bases may be formed.

OXALATE OF ETHULE WITH AMMONIA.

Oxamethane (*Oxalate of Oxide of Ethule and Oxamide*). Syn. Etheroxamide. — Empirical formula, $C_8H_7NO_6$. Oxalic ether is dissolved in alcohol; and alcohol saturated with dry ammoniacal gas is added in small quantities, till a white powder begins to separate. After some hours the clear liquid is filtered from the precipitate, and evaporated, when oxamethane crystallizes, and may be purified by repeated solution and crystallization out of alcohol. It forms colourless transparent scales or plates, with a fatty lustre, melts at about 212°, distils unchanged at about 430°, is soluble in water and alcohol, neutral to test paper, and does not precipitate metallic salts. The aqueous solution, when boiled, is resolved into alcohol, and binoxolate of ammonia. Mixed with excess of ammonia it is instantly converted into oxamide and alcohol.

Explanation.—When to the elements of 2 at. oxalic ether are added those of 1 eq. ammonia, and from the whole are subtracted the elements of 1 at. alcohol, oxamethane is left.

$$\begin{array}{ll} C_{12}H_{10}O_8 & = 2 \text{ at. oxalic ether} \\ +N\ H_3 & = 1 \text{ eq. ammonia} \\ \hline =NC_{12}H_{13}O_8 & \\ -\ C_4H_6O_2 & = 1 \text{ at. alcohol} \\ \hline =NC_8H_7O_6 & = \text{oxamethane.} \end{array}$$

When the oxamethane is again acted on by an excess of ammonia, the same decomposition is repeated. Alcohol is separated, and oxamide is formed.

$$\begin{array}{ll} NC_8H_7O_6 & = \text{oxamethane} \\ +N\ H_3 & = 1 \text{ eq. ammonia} \\ \hline =N_2C_8H_{10}O_6 & \\ -\ C_4H_6\ O_2 & = 1 \text{ at. alcohol} \\ \hline =N_2C_4H_4O_4 & = 2 \text{ at. oxamide.} \end{array}$$

These reactions are easily deduced from the constitution of ammonia and of oxalic acid. The former is $NH_2 + H$, the latter $2CO + O$. Oxalic ether in excess and ammonia yield oxamethane and alcohol, because 1 eq. hydrogen of the ammonia unites with

1 at. oxygen of the oxalic acid forming water, which with half the ether produces alcohol. The third atom of oxygen in the oxalic acid is replaced by amide (amidogen), thus $2CO + NH_2$. This is oxamide, which unites with the half of the oxalic ether to form oxamethane. With an excess of ammonia this portion of oxalic ether undergoes the same decomposition.

BICARBOSULPHATE OF OXIDE OF ETHULE.

XANTHIC ACID.

Syn. Bisulphocarbonate of Oxide of Ethule.— Discovered by Zeise. Formula, $2CS_2 + AeO$. Is not known in the anhydrous state, but only in combination with water or metallic oxides.

Hydrated Xanthic Acid.— Formula, $AeO,2CS_2 + aq.$ Sulphocarbonate of oxide of ethule and potash, (xanthate of potash, see below,) in the dry state, is mixed with dilute sulphuric or hydrochloric acid. After some time a milky liquid is formed, from which, by the addition of more water, the new acid is deposited as a heavy oil, colourless or slightly yellow. It is to be quickly washed with water, and dried by standing over chloride of calcium.

It is an oily liquid, of a peculiar, strong, penetrating, and disagreeable odour, and a weak, acid, bitterish taste. It reddens litmus, but bleaches it after a time. It is very inflammable, burning with a blue flame, is spontaneously decomposed at temperatures above 75°, either alone or in contact with water, producing bisulphuret of carbon, and alcohol. Under water containing absorbed oxygen or air, it becomes opaque and white, and is covered with a thick hard white crust. It decomposes alkaline carbonates with effervescence, the alkali replacing its basic water, and forming a double carbosulphate with the oxide of ethule.

DOUBLE SALTS OF BISULPHURET OF CARBON WITH OXIDE OF ETHULE AND METALLIC OXIDES.

These compounds, the xanthates of Zeise, are analogous in constitution to the preceding compound, Zeise's xanthic acid, the basic water of the latter being replaced by its equivalent of the metallic oxide. The double salts of potash and soda are formed, when, to a solution of potash or soda in alcohol, bisulphuret of carbon is added as long as it is dissolved. The others are obtained by double decomposition. They are insoluble, and have generally a yellow colour; hence the name. When distilled they yield volatile products, both liquid and gaseous; among which Zeise has noticed an amber-coloured oil, of peculiar properties, which he calls Xanthic oil.

The solutions of the soluble xanthates are decomposed by boiling; producing alcohol, bisulphuret of carbon, sulphuretted hydrogen, and a residue consisting of carbonate and hyposulphite of the metal, mixed with sulphur and sulphocarbonate (carbosulphate) of the metallic sulphuret.

These salts, dry or dissolved, may be preserved in close vessels; but they always exhale, when the bottle is opened, the peculiar smell of the bisulphocarbonate of oxide of ethule (xanthic acid). The salts with alkaline and earthy bases are decomposed by acids which combine with the bases. The salts of lead and copper, on the contrary, resist the action of dilute acids, and are hardly decomposed, especially the lead salt, by sulphuretted hydrogen.

Bisulphocarbonate of Oxide of Ethule and Potash. Syn. Xanthate of Potash. — Discovered by Zeise. Formula, $2CS_2$, AeO,KO. Formed, as above-mentioned, by adding bisulphuret of carbon to a saturated solution of fused caustic potash in absolute alcohol as long as it is dissolved.

The liquid commonly becomes semi-solid, when exposed to a cold of 32°, from the separation of fine crystals, which are collected on a filter, washed with ether, pressed in bibulous paper, and dried without access of air. Should no crystals appear, the solution must be concentrated by evaporation at a gentle heat, which is best done in a retort. The pure salt forms colourless or pale yellow anhydrous needles, soluble with a yellow colour in water, of a very bitter peculiar taste. It is soluble in alcohol, insoluble in ether: in a moist atmosphere it is converted into hyposulphite of potash.

Sulphocarbonate of Oxide of Ethule and Suboxide of Copper. Syn. Xanthate of Copper. — When a solution of the preceding salt is mixed with that of a salt of oxide of copper, lemon-yellow flocculi of this double salt are obtained. The oxygen which the oxide of copper loses, in becoming suboxide, produces another compound which adheres to the precipitate. According to Couerbe, it may be removed by ether; and, when pure, has the characters of an oily liquid, solidifying at low temperatures. It appears to contain hydrogen and carbon in the same proportion as in olefiant gas, but no sulphur. According to *Zeise*, the same body is left undissolved when the double salt of copper is dissolved in nitric acid.

OXIDE OF ETHULE AND HYDRATED CYANIC ACID.

Bicyanurate of Oxide of Ethule. Syn. Cyanic Ether.—Formula, $3AeO + 2Cy_3O_3 + 6$ aq. Discovered by Wöhler and Liebig. The vapours of hydrated cyanic acid are conducted into a mixture of equal volumes of alcohol and ether, as long as they are absorbed. The mixture is then allowed to stand for 24 hours, when the new compound separates completely. The crystals are purified from adhering cyamelide by a new crystallization from hot alcohol or water.

It forms colourless, transparent, brilliant needles and prisms; tasteless and inodorous; insoluble in cold water, easily soluble in boiling water or alcohol, sparingly soluble in ether and cold alcohol. Its solution is neutral, and has no action on metallic salts. It melts, when heated, into a colourless liquid, which in a current of air sublimes in vapours, which condense in the air in the shape of a fine light bulky snow. When distilled in a retort, alcohol and water pass over, and cyanuric acid is left. By alkalies it is resolved into alcohol, cyanate of potash, and cyanurate of potash.

OXIDE OF ETHULE AND BENZOIC ACID.

Benzoate of Oxide of Ethule. Syn. Benzoic Ether.—Discovered by Scheele. Formula, AeO,BzO. Four parts of alcohol, sp. g. 0·83, 2 parts of crystallized benzoic acid, and 1 part of concentrated hydrochloric acid, are distilled together. As soon as the product, when mixed with water, becomes milky, the receiver is changed, and the subsequent product is collected. By adding water, the ether is separated; by boiling with water and oxide of lead, it is purified from benzoic acid; and, by standing over chloride of calcium, it is freed from water and alcohol. This ether is also formed when equal volumes of chloride of benzule and alcohol are mixed. The mixture, slightly heated, becomes hot; hydrochloric acid passes off, and by the addition of water the benzoic ether is separated. Here the chloride of benzule acts on the water of the alcohol, producing benzoic and hydrochloric acids; the former of which, in the nascent state, unites with the ether of the alcohol.

Benzoic ether is a colourless oily liquid, having a feeble aromatic smell, like that of fruits, and a pungent aromatic taste. It has a sp. g. of 1·0539 at 50°, boils at 410°, is miscible with alcohol and ether, insoluble in water; is decomposed by chlorine (Malaguti), producing, among other products, chloride of benzule.

COMPOUNDS OF OXIDE OF ETHULE OF UNCERTAIN CONSTITUTION.

Chlorocarbonic Ether.—Formula, $C_6H_5O_4Cl$. When phosgene gas (chlorocarbonic oxide or acid) is mixed with alcohol, a peculiar ethereal liquid is formed to which Dumas has given the above name. Whether it contains ethule, or its oxide, is so far uncertain, that hitherto no compound of ethule, such as alcohol, has been obtained by its decomposition.

Prep.—Absolute alcohol is saturated with phosgene gas, when it becomes hot, and separates into two strata, the lower of which is the new compound. The upper contains water, alcohol, and hydrochloric acid. The new ether is purified by standing over oxide of lead and chloride of calcium, and by rectification. (Dumas.)

Prop.—A colourless, very fluid liquid, of a suffocating ethereal odour, causing a flow of tears; neutral to test paper, of sp. g. 1·133 at 60°, boiling at about 200°; inflammable, burning with a green flame. By warm water it is resolved into hydrochloric acid and other products not yet examined. Concentrated sulphuric acid decomposes it in the cold, producing hydrochloric acid, when heated, with deposition of carbon. Ammonia resolves it into sal-ammoniac and urethane.

If to the elements of 1 at. alcohol we add those of 2 at. phosgene gas, and subtract from the whole those of 1 eq. hydrochloric acid, chlorocarbonic ether is left.

$$\begin{array}{ll} \quad C_4H_6O_2 & = 1\text{ at. alcohol} \\ \underline{+C_2\quad O_2Cl_2} & = 2\text{ at. phosgene gas} \\ =C_6H_6O_4Cl_2 & \\ \underline{-\quad H\quad Cl} & = 1\text{ eq. hydrochloric acid} \\ =C_6H_5O_4Cl & = 1\text{ at. chlorocarbonic ether.} \end{array}$$

Dumas considers it as a compound of a peculiar acid with ether, which acid may be regarded as carbonic acid in which part of the oxygen has been replaced by its equivalent of chlorine.

$$C_2\left.\begin{matrix}O_3\\Cl\end{matrix}\right\}+C_4H_5O=C_6H_5O_4Cl.$$

Berzelius considers it a compound of carbonic ether with phosgene gas. $C_5H_5O_3+COCl$.

Urethane.—Formula, $C_6H_7O_4N$. Discovered by Dumas.

Prep. — Chlorocarbonic ether is dissolved in aqua ammoniæ, when an instantaneous reaction ensues with developement of heat. The solution is evaporated to dryness in vacuo over sulphuric acid, and the dry residue distilled in a gentle heat. Urethane passes over as a colourless liquid, which consolidates on cooling, while sal-ammoniac is left behind.

Prop. — Colourless, pearly, crystalline mass, like spermaceti; fusible at 212°, volatile without change at 365°; soluble in water and alcohol, from which, by spontaneous evaporation, it separates in large crystals. Its aqueous solution has no action on metallic salts. If heated in the moist state, it is decomposed with disengagement of ammonia. Is decomposed by alkalies, the products not yet examined. In urethane the chlorine of chlorocarbonic ether is replaced by amide: $C_6H_5O_4 + NH_2$. When the ether is acted on by ammonia, the chlorine with 1 eq. of hydrogen from ammonia forms hydrochloric acid, which combines with the ammonia in excess to form sal-ammoniac. The amide, derived from the ammonia that has lost 1 eq. hydrogen, takes the place of the chlorine. It may be considered as a compound of 2 at. carbonic ether, and 1 at. urea, $2(C_5H_5O_3) + C_2N_2H_4O_2 = 2(C_6H_7O_4N)$. Hence the name compounded of urea and ether. It has also the composition of anhydrous lactate of ammonia, a substance not yet obtained in a state of purity.

TRANSFORMATIONS AND PRODUCTS OF THE DECOMPOSITION OF ETHULE AND ITS COMPOUNDS.

If the vapours of ether or alcohol be passed through a red-hot tube, they are resolved into inflammable gases, aldehyde, and water. The gases are mixtures of olefiant gas and light carburetted hydrogen, in which the carbon is to the hydrogen, in atoms, as 4 to 5; exactly the proportion existing in ethule.

The empirical formula of aldehyde is $C_4H_4O_2$, and from its production it follows that 2 at. ether have given up their oxygen to a third atom. The two first atoms are resolved into olefiant gas and light carburetted hydrogen; the third, + 2 at. oxygen from the other two, yields aldehyde and water.

$$\begin{array}{ll}
C_8\,H_{10} & = \text{olefiant gas, and light carb. hyd.} \\
C_4\,H_4\,O_2 & = \text{aldehyde.} \\
\quad H\;\;O & = \text{water.} \\
\hline
C_{12}H_{15}O_3 & = \text{3 at. ether.}
\end{array}$$

According to this explanation, the two carbo-hydrogens should be to each other, in volumes, as 3 to 2. Further, 2 at. ether can be resolved into 1 at. aldehyde, 2 at. olefiant gas, and 2 at. light carburetted hydrogen.

$$\begin{array}{lll} C_4 & H_4 & O_2 = 1 \text{ at. aldehyde.} \\ C_2 & H_4 & = 2 \text{ at. light carbo-hydrogen.} \\ C_2 & H_2 & = 2 \text{ at. olefiant gas.} \\ \hline C_8 & H_{10} & O_2 = 2 \text{ at. ether.} \end{array}$$

In this case, the volume of the light carbo-hydrogen would be to that of the olefiant gas as 2 to 1; and the combustion of the mixture should yield for 4 at. carbonic acid 6 at. water.

All the decompositions which ether in other proportions undergoes at high temperatures are similar to the above; only that the products vary. On the one hand are formed bodies containing all the oxygen; on the other, carbo-hydrogens.

According to Masson and Dumas, when fused chloride of zinc is dissolved in alcohol, there is formed a hydrated compound of chloride of zinc with ether, which at 284° is resolved into ether which is disengaged, and water which evaporates in the gaseous ether. The ether and water are found in the receiver uncombined. If there is a great excess of chloride of zinc, the ether, at temperatures from 320° to 360°, is resolved into water and two carbo-hydrogens of unequal volatility; one boiling at 570°, the other at 212°. The composition of the latter is C_8H_7; and that of the former, the less volatile, is C_8H_9. Both together, $= C_{16}H_{16}$, have exactly the composition of olefiant gas. Consequently, in their formation, 4 at. ether have been resolved into 4 at. water and these two carbo-hydrogens.

When ether is prepared from alcohol and sulphuric acid, and the raw ether in large quantity is rectified with milk of lime, there is left in the retort, swimming on the surface of the liquid, an oil, long known as the oil of wine. It is highly probable that it is a mixture of the two carbo-hydrogens just described. It is a yellow, viscid oil of an aromatic odour, sp. g. 0·9174 at 50°, soluble in ether, sparingly soluble in alcohol and water. It is altered by exposure to the air, becoming thick like turpentine. It is rendered white and resinous by chlorine, with formation of hydrochloric acid. Aqua potassæ renders it brown, oil of vitriol turns it black, but on the addition of water a colourless oil separates. The raw oil yielded to Dumas carbon and hydrogen in the proportion of $C_{16}H_{15}$; which result has been confirmed by Liebig.

Sulphate of Oxide of Ethule and Etherole.— Syn. Sulphovinate of Etherole; Heavy Oil of Wine.—The nature and constitution of this long-known substance were first clearly ascertained by Serullas.

Formula, $2SO_3 + C_8H_9O$.

This oil is formed by the decomposition of the neutral sulphate of oxide of ethule, a compound which cannot exist in the separate state. It is always formed when ether and anhydrous sulphuric acid directly or indirectly come in contact. If anhydrous ether be saturated with anhydrous sulphuric acid, the former is instantly resolved into alcohol, which separates, and a compound of oxide of ethule and etherole. Both products combine with sulphuric acid, and there are formed bisulphate of oxide of ethule with 1 at. water, and sulphate of oxide of ethule and etherole. Four at. sulphuric acid $4SO_3$, and 3 at. oxide of ethule $C_{12}H_{15}O_3$, yield 1 at. bisulphate of oxide of ethule $2SO_3,C_4H_5O,HO$, and 1 at. of the new oil $2SO_3,C_8H_9O$. Thus from 2 at. ether is separated 1 at. water, which combines with 2 at. sulphuric acid and 1 at. ether. Along with the above products there are formed, by a different reaction, ethionic and isethionic acids. If the liquid be mixed with water, the excess of ether is separated; the sulphate of oxide of ethule and etherole is dissolved in it, and may be obtained by evaporating the ether, while the bisulphate and the two acids combine with the water.

When sulphovinate of lime or potash is subjected to dry distillation, there are obtained the oil under consideration, alcohol, sulphurous acid, and olefiant gases, and a residue composed of carbon and a sulphate. These products are formed by two independent and simultaneous reactions. From 2 at. double sulphate of oxide of ethule and lime are obtained 1 at. of the oil, 1 at. water, and 2 at. sulphate of lime. In the other reaction, the same materials yield the following products, along with 2 at. sulphate of lime.

$$\begin{array}{llllll}
\text{2 at. sulphurous acid} = & S_2 & & & O_4 & \\
\text{1 at. alcohol . .} = & & C_4 & H_6 & O_2 & (C_4H_5O+\text{aq.}) \\
\text{2 at. olefiant gas .} = & & C_2 & H_2 & & \\
\text{2 at. water . . .} = & & & H_2 & O_2 & \\
\text{2 at. carbon . .} = & & C_2 & & & \\
\hline
 & S_2 & C_8 & H_{10} & O_8 = 2SO_3+2(C_4H_5O). &
\end{array}$$

By the addition of a dry fixed base, such as lime or baryta, one of these reactions is prevented. In this case there are formed sulphate of oxide of ethule and etherole, and hydrate of lime, which, with an atom of sulphate of oxide of ethule, produces sulphate of lime and alcohol. Three at. double sulphate of oxide of ethule and lime, $6SO_3 + C_{12}H_{15}O_3 + 3CaO$, with 1 at. lime, CaO, give

4 at. sulphate of lime	=	$4SO_3$				$4CaO$
1 at. alcohol	=		C_4	H_6	O_2	
1 at. sulphate of oxide of ethule and etherole	=	$2SO_3$	C_8	H_9	O	
		$6SO_3$	C_{12}	H_{15}	O_3	$4CaO$

To obtain this substance, an intimate mixture of dry sulphovinate of lime or potash with its own weight of quick lime is distilled at a temperature not higher than about 540°. The product is freed from alcohol by evaporation in the air or in vacuo over sulphuric acid. This oil may likewise be obtained by distilling the basic sulphovinate of lead.

It is a colourless, oily liquid; heavier than water, sp. g. 1·133; of an aromatic ethereal odour, and a cooling taste; without action on dry vegetable colours. It boils at 540°, distilling unchanged when dry; potassium at the ordinary temperature is not tarnished in it, but decomposes it at a higher temperature. It is miscible with alcohol and ether.

In contact with water or alkalies it is decomposed, producing hydrous bisulphate of oxide of ethule, and etherole. Heated with sulphuret of potassium it gives mercaptan, and a heavy oil containing sulphur. (Zeise.)

ETHEROLE AND ETHERINE.

Etherole. Syn. Light Oil of Wine.—A product of the decomposition of the substance last described. Discovered by Hennell; but most accurately studied by Serullas, according to whom it contains carbon and hydrogen in the same proportions as olefiant gas. This has lately been confirmed by Marchand.

Prep.—The heavy oil of wine is gently heated with water, and the light oil which separates is washed with water till all acid is removed. It is dried by chloride of calcium.

Prop.—A colourless, oily liquid, of sp. g. 0·917 to 0·920; boils at 536°, becomes viscid at − 13°, and solid at − 31°; sparingly soluble in rectified spirits, very soluble in absolute alcohol and ether; miscible in all proportions with oil of vitriol, and separated unchanged by water: combines with anhydrous sulphuric acid, becoming brown; water separates nothing, and the acid liquid, neutralized by baryta, gives a salt which Marchand considers to be ethionate of baryta.

When etherole is left for a long time at a low temperature, it deposits crystals of etherine. Etherine, or camphor of oil of wine, has the same composition as etherole or olefiant gas, in 100 parts. When the etherole refuses to deposit more crystals in the cold, those deposited are pressed between folds of bibulous paper, and purified by solution in ether and crystallization.

Prop.—Brilliant, long, translucent, tasteless, friable prisms and plates; fusible at 230°, boiling at 500°; sp. g. 0·980; soluble in alcohol and ether, insoluble in water.

ETHIONIC AND ISETHIONIC ACIDS.

These two acids, one of which is remarkable on account of its extreme stability, were first obtained by Magnus, by bringing in contact, in the cold, alcohol and anhydrous sulphuric acid. The resulting liquid is diluted with water, and neutralized by carbonate of baryta. There is formed, along with sulphate of baryta, which is separated by the filter, ethionate of baryta, which remains dissolved. If the solution be evaporated by a gentle heat to the consistence of syrup, and mixed with alcohol, it deposits ethionate of baryta in the form of a white powder. By the cautious addition of diluted sulphuric acid to the aqueous solution of this salt, a solution of ethionic acid may be obtained. This acid has little permanence. If its solution be boiled, the liquid contains free sulphuric acid and isethionic acid. This latter acid is also obtained by saturating pure ether with anhydrous sulphuric acid. When water is added to the mixture, the excess of ether separates, along with heavy oil of wine ($2SO_3,C_8H_9O$). The liquid below the stratum of ether is acid, and when heated gently yields ether; when boiled, alcohol, which is thus reproduced from ether directly. The residual liquid after the boiling contains free sulphuric acid and isethionic acid.

The formation of both these acids has lately been explained by Magnus. Alcohol is decomposed by anhydrous sulphuric acid, and the compound formed is sulphate of etherole, $4SO_3 + C_4H_4$. Regnault has found that this compound can be directly produced by saturating anhydrous sulphuric acid with olefiant gas. White fusible crystals are formed, which, when dissolved in cold water, combine with one atom of water, and form ethionic acid, $4SO_3$,

C_4H_5O. By boiling this solution the ethionic acid loses 2 atoms of sulphuric acid, and is converted into isethionic acid, $2SO_3,C_4H_5O$. This discovery enables us to explain the action of dry sulphuric acid on alcohol and ether without ambiguity.

The first effect of the anhydrous acid on alcohol is to form hydrated bisulphate of oxide of ethule. An excess of the acid decomposes the combined oxide of ethule, depriving it of the elements of water, by which means etherole, or a substance of the same composition is set free; which, with 4 at. sulphuric acid, produces ethionic acid and water.

$S_2O_6+C_4H_5O$ bisulphate of oxide of ethule, plus 2 at. sulphuric acid, —1 at. water, $+\underline{S_2O_6-H\ O}$
gives . . $S_4O_{12}+C_4H_4$ = the elements of the substance discovered by Regnault.

Pure ether with anhydrous sulphuric acid gives water and heavy oil of wine ($2SO_3,C_8H_9O$). The water combines with the sulphuric acid to form hydrated acid, which, with another portion of ether forms bisulphate of oxide of ethule ($2SO_3,HO,C_4H_5O$). By the action of anhydrous sulphuric acid on the etherole there is produced just as with olefiant gas, which is isomeric with etherole, the substance which, in contact with water, forms ethionic acid; and, by the further action of the anhydrous acid on the bisulphate of oxide of ethule, the same reaction occurs as with alcohol.

Under all circumstances, therefore, a mixture of alcohol or ether with anhydrous sulphuric acid contains bisulphate of oxide of ethule, and a new substance, (produced by the action of sulphuric acid on a carbo-hydrogen,) which, with water, forms ethionic acid. If the liquid is boiled, the bisulphate is resolved into alcohol and sulphuric acid; the ethionic acid into sulphuric acid and isethionic acid. If it be neutralized with baryta before being boiled, we obtain ethionate of baryta and the double sulphate of oxide of ethule and baryta. When this solution is evaporated at temperatures lower than 212°, till crystals begin to appear, on adding absolute alcohol, crystals of ethionate of baryta are precipitated, which, by being redissolved in water and again precipitated by alcohol, are rendered perfectly pure. Ethionate of baryta consists of $4SO_3,C_4H_5O,BaO$, and from it all the other salts of ethionic acid can be easily made.

Isethionic acid is obtained by cautiously adding dilute sulphuric acid to isethionate of baryta, till all the baryta is precipitated. The filtered liquid is evaporated, at first with the aid of heat, afterwards in vacuo over sulphuric acid. It is a viscid oily liquid of a very sour taste, very soluble in alcohol and ether. It bears a temperature of 302° without decomposition. At a higher temperature it is blackened. When a salt of isethionic acid is fused with a hydrated alkali, it yields free hydrogen, with carbonate and oxalate of the base, the carbon being derived from the organic part of the acid; a mixture of equal equivalents of sulphate and sulphite of potash is also formed. This last character is peculiar to the hyposulphates. It is, therefore, probable, that the true formula of the isethionic acid must be $S_2O_5,C_4H_5O_2 + aq$.

The salts of isethionic acid are without exception soluble in water. The acid decomposes the salts of all organic acids, uniting with the base. It also decomposes the chlorides of the alkalifiable metals with the aid of heat, disengaging hydrochloric acid. Its salts are all neutral, and bear a heat of 480° without decomposition. The *Isethionate of ammonia* crystallizes in octohedrons. *Isethionate of potash* forms anhydrous, colourless, transparent broad plates. *Isethionate of copper*, sea-green regular octohedrons, containing 2 at. water of crystallization, which are expelled by a heat of 230°, when the crystals become milk-white. *Isethionate of silver* is very soluble, and crystallizes in brilliant broad plates. *Isethionate of lead* crystallizes in hard anhydrous needles, formed in radiated groups.

Isethionate of baryta.—Formula, $S_2O_5,C_4H_5O_2,BaO$.

Prep.—Anhydrous sulphuric acid is placed in a U shaped tube, and olefiant gas is made to pass through it. At first it is kept cold, afterwards it is warmed, but only to the melting point of the acid. The olefiant gas must be first passed through milk of lime to remove sulphurous acid, and afterwards through oil of vitriol to retain water. As soon as no more gas is absorbed, the mass is dissolved in water, boiled for half an hour in the diluted state, saturated with carbonate of baryta, filtered, and evaporated till it crystallizes. Or anhydrous ether, carefully cooled, is saturated with anhydrous sulphuric acid, the mixture diluted with water, when ether and heavy oil of wine separate; the acid solution is boiled as long as alcohol is given off, neutralized with carbonate of baryta, and evaporated. The salt crystallizes easily out of a very strong solution in opaque six-sided plates, which are anhydrous, permanent in the air, fusible at 392°, decomposed with frothing at a higher temperature.

When, in saturating ether with anhydrous sulphuric acid, it is not kept sufficiently cool, sulphurous acid is disengaged, the mixture blackens and is found to contain an acid different from isethionic acid, distinguished by forming with baryta a salt totally insoluble in alcohol, which crystallizes along with the isethionate of baryta, but is easily removed by alcohol. This acid has been named

Methionic Acid.—Formula of the anhydrous acid, as it exists in the salt of baryta, $S_2C_2H_3O_7$. It may be obtained from the methionate of baryta, in the same way as isethionic acid from isethionate of baryta. It is a very sour liquid, which may be boiled and evaporated without decomposition.

Methionate of Baryta.—When ether is saturated with anhydrous sulphuric acid at the ordinary temperature, and the mixture treated as above, the solution contains isethionate and methionate of baryta. When nearly about to crystallize, it is mixed with its own bulk of alcohol, which precipitates the methionate. It may be purified by solution in water and crystallization. It forms colourless, transparent, brilliant, anhydrous scales, like chlorate of potash; soluble in 40 parts of cold water, more soluble in hot water. The solution precipitates no metallic salts; the salt is insoluble in alcohol, loses no weight at 212°; and when heated assumes a fugitive yellow colour, yields water, sulphurous acid, and sulphur. The residue contains sulphate of baryta. It is decomposed by fusion with caustic potash, but the residue contains no sulphite of potash.

Althionic Acid.—When the residue of the preparation of olefiant gas from alcohol and sulphuric acid is diluted with water, and neutralized with milk of lime, a salt of lime remains in solution, which may be evaporated and crystallized without alteration. If the lime be removed from the solution of this salt by oxalic acid, a sour liquid is obtained, which when boiled yields alcohol, and then is found to contain free sulphuric acid. Regnault has named this acid Althionic acid. This reaction when heated is identical with that of sulphovinic acid (bisulphate of oxide of ethule); and the salts, which the acid forms with bases, are exactly of the same composition as the sulphovinates. They were considered to be the same, till Ettling pointed out marked differences in the crystalline form of the salts of the two acids with the same bases; an observation confirmed by Regnault. The salts of potash, lime, and baryta crystallize with much greater difficulty than the corresponding sulphovinates. The most marked distinction is perceived in the salt of copper. The sulphovinate of that base (double sulphate of oxides of ethule and copper) crystallizes in large azure-blue rectangular prisms or eight-sided tables; the althionate of copper in long thin rhombic plates, the acute angle of which $=60°$, of a pale green colour.

The althionate of baryta, when boiled for a long time, deposits sulphate of baryta, and the liquid becomes very acid. If now saturated with carbonate of baryta, more sulphate is formed, and there remains in solution a small quantity of a soluble salt of baryta not further examined.

It is hardly to be doubted, that the difference in the properties of the so-called althionates and the double sulphates of ethule and bases depend on a similar cause to that which produces the difference between the ethionates and those same salts; that is, the althionates must be double salts of isethionic acid, or an acid of the same composition, and the acid of the sulphovinates.

Products of the Oxidation of Ethule and its compounds, in which the number of atoms of Carbon remains the same as in Ether and Alcohol.

1. ACETULE AND ITS COMPOUNDS WITH OXYGEN.

It has already been mentioned, that when nitric acid acts on ether or alcohol, different products are obtained, besides the oxides and acids of nitrogen, according to the proportion of oxygen which enters into combination with the elements of the ethule. These are, aldehyde, acetic acid, formic acid, oxalic acid, carbonic acid, and water. The elements of ethule possess different degrees of attraction for oxygen, the hydrogen combining more easily with it than the carbon; whence it happens, that in the earlier stages of its action it is the hydrogen which is principally oxidized, and removed, or replaced by oxygen. By the use of different oxidizing agents, these products vary in their number, that is, in the number of those simultaneously formed; but they do not vary in their mode of formation. By the slow oxidation of alcohol, by means of the oxygen of the atmosphere, in the process for forming acetic acid now often employed, water, aldehyde, and acetic acid are the only products. In this case 2 at. oxygen combine with 2 at. hydrogen of the ether, producing aldehyde, which takes up directly two more atoms of oxygen, forming acetic acid.

$$\begin{array}{l} \ C_4H_5O+\text{aq.}=\text{alcohol,} \\ -\ \ H_2 \qquad +O_2=2HO \\ \hline \ C_4H_3O+\text{aq.}=\text{aldehyde, oxide of acetule,} \\ +\qquad O_2=\ 2\ \text{at. oxygen.} \\ \hline \ C_4H_3O_3+\text{aq.}=\text{hydrated acetic acid.} \end{array}$$

By the use of more powerful oxidizing agents, as a mixture of hyperoxide of manganese or bichromate of potash with dilute sulphuric acid, or the contact of red-hot platinum with the vapour of alcohol and ether, oxygen being also present, there are formed products of the oxidation of aldehyde, namely, aldehydic acid and acetic acid; and further, products of the oxidation of these, as formic and carbonic acids. By the action of nitric acid oxalic acid is formed, which remains in the residue of the distillation. Acetic and formic acids combine easily with oxide of ethule: hence acetate and formiate of oxide of ethule always accompany these products; and, when nitric acid is the oxidizing agent, hyponitrite of oxide of ethule is also formed.

When the vapour of alcohol, mixed with oxygen or air, is put in contact with spongy platinum or platinum powder, another substance is formed, namely, acetal; which must be considered as a compound of aldehyde and oxide of ethule.

ACETULE.

By the subtraction of hydrogen from ethule there is produced a new radical, which is named acetule. Aldehyde may be considered as the hydrate of the first stage of oxidation of this radical. This oxide is not, like oxide of ethule, a base; but has rather a well-marked character as an acid-forming oxide, having itself feeble acid properties, and forming a crystalline compound with ammonia. It absorbs oxygen greedily from the atmosphere, and is converted into hydrated acetic acid. By treating its solution in water with oxide of silver, another acid, containing less oxygen than acetic acid, is produced, which is named aldehydic acid. The compounds of acetule with oxygen are—

Acetule	C_4H_3	unknown.
Oxide of acetule	C_4H_3O	
Hydrate of oxide of acetule .	C_4H_2O	+aq. aldehyde.
Acetulous acid	$C_4H_3O_2$	+aq. aldehydic acid.
Acetulic acid	$C_4H_3O_3$	+aq. acetic acid.

HYDRATE OF OXIDE OF ACETULE. ALDEHYDE.

Doebereiner observed, that by distilling sulphuric acid, alcohol, and oxide of manganese, a liquid was obtained, which, if mixed with potash, and warmed, became brown; and that from the brown solution acids precipitated a reddish-brown resinous substance. The substance which gave rise to these phenomena was first obtained by Liebig. It is aldehyde.

Prep.—Two parts of aldehydammonia are dissolved in 2 parts of water, and mixed with a cold diluted acid, made with 3 parts of oil of vitriol and 4 parts of water. The mixture is distilled in a retort, connected with a condenser surrounded by ice, with the heat of the water-bath. The product is twice rectified with its own bulk of chloride of calcium, at a temperature from 77° to 86°, and is then pure.

Prop.—A colourless clear liquid, refracting light feebly, of a peculiar ethereal and suffocating smell. It boils at 72°. Sp. g. at 65°, 0·79. It is miscible with water, alcohol, and ether, neutral to test paper, inflammable, burning with a pale flame. It absorbs oxygen, and is converted into hydrated acetic acid; dissolves phosphorus, sulphur, and iodine; is decomposed by chlorine and bromine. Solution of chlorine converts it into acetic acid. The same change takes place when it is heated with dilute sulphuric acid. When mixed with oil of vitriol, it becomes thick and brown, and after some time a black carbonaceous coagulum separates. When mixed with aqua potassæ, the mixture soon becomes brown, and after some time a light brown resin rises to the surface. When a solution of aldehyde is warmed with oxide of silver, the oxide is partially reduced, without disengagement of gas, and the vessel is thus covered with a brilliant surface of silver. The liquid contains aldehydate of silver. A liquid containing aldehyde, to which some ammonia is first added, and then nitrate of silver, till all alkaline reaction disappears, produces the same appearance of reduced metal when heated; and this, with the action of potash, is a sure and simple method of proving the presence of aldehyde in any liquid. When long kept, aldehyde spontaneously changes into two substances of the same composition: one of which, metaldehyde, is solid at ordinary temperatures; the other, elaldehyde, is a liquid.

Formula of aldehyde, $C_4H_3O + aq$.

Aldehydammonia.—Doebereiner observed that raw acetal, saturated with ammonia, deposited crystals; in which Liebig proved the presence of aldehyde.

Formula, C_4H_3O,NH_3,HO.

Prep.—Six parts of sulphuric acid, mixed with 4 of water, 4 of alcohol at 80 p. c., and 6 of hyperoxide of manganese in fine powder, are distilled by a gentle heat. The retort must be capacious, and connected, air-tight, with a receiver surrounded by ice. When no more frothing is observed in the retort, the product, which amounts to 6 parts, is rectified with its own weight of chloride of calcium. The product now amounts to 3 parts, and is again rectified with its own weight of chloride of calcium. In this way $1\frac{1}{2}$ parts are obtained of a liquid, consisting chiefly of aldehyde, with a little water, alcohol, and acetic and formic ethers. These $1\frac{1}{2}$ parts are mixed with their bulk of ether, and the mixture is saturated with dry ammoniacal gas, when crystals of aldehydammonia separate in abundance; which, when washed with ether and dried at the ordinary temperature, are quite pure.

Prop.—Colourless, transparent, brilliant, acute rhombic prisms, refracting light powerfully, friable, having an odour of turpentine; fusible between 158° and 176°, distilling unchanged at 212°. The crystals become brown by exposure to the air, and even in sealed tubes, and acquire a smell of burnt feathers. They are very soluble in water, and the solution has an alkaline reaction. They are soluble in alcohol, acetal, and acetic ether; insoluble in ether. A concentrated solution gives, with nitrate of silver, a precipitate soluble in water, insoluble in alcohol, which contains nitric acid, oxide of silver, ammonia, and aldehyde.

ACETAL.

Discovered by Doebereiner, and by him named oxygen ether.

Prep.—In a tall wide-mouthed bottle, containing alcohol to the depth of an inch, are suspended 3 or 4 watch-glasses, containing powder of platinum to the depth of 2 lines, near the surface of the liquid. The platinum should be moistened with water, and the bottle left for some months in a warm place. The liquid is then found to be very acid, and to contain acetal, aldehyde, acetic acid, and acetic ether. It is neutralized with chalk, and distilled. The product is treated with repeated portions of chloride of calcium till it is no longer moistened. The liquid is then rectified; and as soon as the boiling point rises to 202°, the product is pure acetal.

Prop.—A colourless, mobile liquid, of a peculiar smell, like that of Hungary wines; boiling at 204°; sp. g. at 68°, 0·823. Soluble in 6 parts of water, miscible in all proportions with alcohol. Is not rendered brown by potash at first; but the mixture absorbs oxygen, and then becomes brown, resin of aldehyde being formed. It is rendered thick and black by oil of vitriol. Its empirical formula is $C_8H_9O_3$. According to which, it may be considered a compound of 3 at. oxide of ethule and 1 at. acetic acid $= C_{16}H_{18}O_6$. But the action of potash and sulphuric acid seems to prove incontestably the presence of aldehyde; and its probable rational formula is therefore C_4H_3O,AeO,HO, a compound of aldehyde and oxide of ethule.

PRODUCTS OF THE DECOMPOSITION AND TRANSFORMATION OF ALDEHYDE.

Aldehyde with Potassium.—When potassium is introduced into aldehyde, heat is developed, hydrogen gas is disengaged, and a solid compound is formed, containing potash, which is soluble in water, has an alkaline reaction, reduces the salts of silver with the aid of heat, and is decomposed by acids, without yielding aldehyde. This compound has not been minutely examined; it is probably aldehydate of potash, or contains that substance.

Resin of Aldehyde.—A product of the decomposition of the aqueous solution of aldehyde by caustic potash. It is likewise produced when an alcoholic solution of potash is exposed to the atmosphere. The reaction has not been fully studied, yet it is known that the resin of aldehyde is not the only product. A mixture of potash with aldehyde and water, when heated, gives off a combustible liquid, of a most penetrating odour, which smarts the eyes very powerfully, the composition of which is unknown. The resin swims on the surface of the liquid in the retort, in the shape of a soft light-brown mass, very soluble in alcohol and aqua potassæ, from which it may be obtained by evaporation, or by saturating with an acid. When dried and heated to 212°, it gives off a very nauseous soapy smell, and it sometimes happens that it inflames spontaneously.

Elaldehyde.—Isomeric, or rather polymeric with aldehyde. When pure aldehyde is long kept, it loses by degrees its solubility in water, and produces two new substances. If kept at 32°, it forms ice-like needles, which melt at about 35° into a transparent liquid, lighter than water. It has the odour of aldehyde, but weaker; it boils at 201·5°. It does not become brown with potash, nor does it act on nitrate of silver. It does not combine with ammonia. Its composition in 100 parts is exactly that of aldehyde, but the density of its vapour shows that 3 vol. of vapour of aldehyde have been condensed into one volume of elaldehyde.

Empirical formula, $C_{12}H_{12}O_6$. (Fehling.)

Metaldehyde.—When aldehyde is kept at the ordinary temperature, it is partially converted into crystals of metaldehyde, which sometimes disappear without apparent cause. It forms long, hard, four-sided prisms, friable, volatile at 230° without previously melting. The vapour condenses in the air in the form of a light snow. It is insoluble in water, soluble in alcohol, out of which it may be crystallized. It has also the same composition in 100 parts as aldehyde; but doubtless the density of its vapour is different, although that is not yet ascertained. (Fehling.)

From the great tendency of aldehyde to be converted into bodies possessing different properties, probably arises the circumstance, that, by the action of chlorine on it, many new compounds are formed, which are quite different from those produced in alcohol by the same agent. Some experiments, made with the view of forming chloral from aldehyde, succeeded so far as to produce a liquid having most of the properties of chloral; but in many other experiments substances totally different were obtained. But the fact that chloral (as will be shown hereafter), as well as aldehyde, is prone to undergo spontaneous conversion into a compound isomeric or polymeric with itself, without the aid of any reagent, is strong proof of an analogy in the constitution or internal molecular arrangement of these two substances.

Aldehydic Acid. Syn. Acetulous Acid. Lampic Acid.—The name of aldehydic acid has been given to the acid which is formed when an aqueous solution of aldehyde is warmed with oxide of silver. In this case, as above mentioned, part of the oxide of silver is reduced, and the rest combines with the new acid. If a current of sulphuretted hydrogen be passed through the liquid, the silver is separated as sulphuret, and the aldehydic acid is obtained pure, but much diluted. It is sour, and neutralizes metallic oxides; but its salts cannot be obtained pure, because when evaporated they pass into acetates, with the deposition of a brown substance resembling the resin of aldehyde. In vacuo they are obtained of a yellow colour. Their characteristic property is to yield with cold sulphuric acid a vapour which attacks the eyes strongly, while the mixture becomes black. If a solution of aldehydate of baryta be warmed with oxide of silver, or of mercury, these metals are reduced without effervescence, and the solution is found to contain pure acetate of baryta. The following considerations leave no doubt as to the composition of this acid:—

Aldehyde, gently warmed with oxide of silver, gives metallic silver and a soluble salt of oxide of silver. The latter may be safely assumed to contain 1 at. oxide of silver. If now the solution of this salt be mixed with as much barytic water as precipitates all the oxide of silver, and the solution, which now contains the acid combined with baryta, be heated along with the oxide of silver just formed, the latter is completely reduced, and the liquid now contains pure acetate of baryta. In this salt the oxygen of the acid is to that of the base as 3 : 1; but 1 of these 3 at. of oxygen was combined with oxide of silver in the aldehydate, the salt first formed, and passed from the silver to the aldehydic acid, converting it into acetic acid. Now acetic acid in its dry salts has the formula $C_4H_3O_3$; consequently the dry aldehydic acid must have the formula $C_4H_3O_2$, or in the state of hydrate $C_4H_3O_2 + aq$.

Aldehydic acid is in all probability one ingredient of the so-called lampic acid, discovered by Davy and Faraday, and more closely examined by Daniell and Arthur Connell. When a coil of platinum wire is kept red-hot in the wick of a spirit-lamp, and the products of this imperfect combustion condensed in a proper apparatus, an acid liquid is obtained, the vapour of which acts strongly on the eyes, and which contains several acids, one of which is formic acid. (Connell.) Daniell neutralized this acid liquid, which he called lampic acid, with alkalies, and obtained salts, the composition of which approached nearly to that of acetates, but which differed from them by their action on the salts of silver and mercury; the solutions of which, heated with the new salts, deposited reduced metal, with disengagement of carbonic acid gas, while a part of the oxides was found dissolved in the form of acetates. This induced Connell to pronounce the lampic acid a mixture of acetic and formic acids: but the solutions of its alkaline salts become brown by evaporation, and the acid itself is blackened by sulphuric acid; characters which do not belong to either acetic or formic acids, but rather to aldehydic acid. Besides, acetic and formic acids, although both have a pungent smell, do not affect the eyes, which the lampic acid does, and which is remarkably the case with aldehydic acid. Hence it is probable that lampic acid is a mixture of aldehydic, acetic, and formic acids. A part of the acetic acid obtained from it is probably formed from aldehydic acid as above. A comparison of the lampic acid with the aldehydic acid prepared directly from aldehyde, will soon decide the question.

ACETYLIC ACID.—ACETIC ACID.

Vinegar has been known from the earliest periods, and pure hydrated acetic acid was first obtained by Löwitz in 1793. All liquids which are capable of the vinous fermentation may be made to produce vinegar. In all such liquids sugar is present, which is first, by fermentation, converted into alcohol, and afterwards, by oxidation, into acetic acid.

The process was called the acetous fermentation, but has nothing in common with the true vinous fermentation; for in the latter the operation, once begun, goes on in close vessels, while the presence of oxygen or air is throughout essential to the former. The nature of the acetification of alcohol was first clearly developed by Doebereiner, from a consideration of the very remarkable fact, observed by E. Davy, that the vapour of alcohol, in contact with platinum powder, caused the powder to become red-hot, and was itself converted into acetic acid. Doebereiner showed that oxygen is essential in this experiment, and further proved that 1 at. alcohol, to form acetic acid, absorbed 4 at. oxygen. The composition of acetic acid being known, it followed that these elements must yield 1 at. dry acetic acid and 3 at. water. $C_4H_6O_2 + O_4 = C_4H_3O_3 + 3HO$.

The way in which this change occurs has been already explained under acetule (see p. 868).

In the ordinary mode of preparing vinegar certain substances are necessary, the nature and precise action of which are still obscure, such as ferment or similar matters; but it is certain that they only act in contributing to the conversion of alcohol into acetic acid, by virtue of the power they possess of causing the alcohol to absorb oxygen from the air.

Pure alcohol, or spirits free from all impurity but water, does not become acid by exposure to the atmosphere; while in fermented liquids, the alcohol, being mixed with various organic matters, when placed in a proper temperature, quickly disappears, and is replaced by acetic acid. The same takes place with alcohol, to which have been added certain organic substances, such as extract of malt, honey, wine, lees of wine, yeast, or even ready-made vinegar. From a careful consideration of all the phenomena, it is evident that these substances act the same part in the oxidation of alcohol, as the deutoxide of nitrogen does in the oxidation of sulphurous acid, in the manufacture of sulphuric acid. They absorb, namely, oxygen from the atmosphere, and transfer it to the alcohol. De Saussure has shown that almost all organic substances, as well as platinum, absorb a mixture of oxygen and hydrogen, causing them to unite and form water. Let alcohol be substituted for the hydrogen, and we see at once how acetic acid may be formed by the acid of organic substances. These substances, unlike the platinum, however, are themselves altered by degrees, and converted into substances insoluble in water. When this change is produced at a temperature at which the alcohol is not oxidized, the liquid, by the removal of these substances, loses its power of forming vinegar in a higher temperature. This often happens in wine; and Bavarian beer is a beer which has been made to ferment at a low temperature till all the matters which favour acetification have been rendered insoluble.

Some have been disposed to ascribe the acetification of alcohol to a new force, called Catalysis, whereby the mere contact of certain bodies causes combinations and decompositions. But the same view would be applicable to the action of deutoxide of nitrogen in the manufacture of sulphuric acid, were it not that the changes of colour in the formation and decomposition of nitrous acid betrayed the real nature of the change. There is no occasion, therefore, to have recourse to a new and mysterious power, as it is very plain that the organic matters alluded to promote the acetification, as the powder of platinum does, by absorbing oxygen from the atmosphere, and condensing it so far that the alcohol is enabled to combine with it. The foregoing remarks will serve to explain the theory of ordinary acetification, or the making of vinegar.

On the small scale, 100 parts of water, 13 of brandy, 4 of honey, and 1 of winestone or tartar, or 120 parts of water, 12 of brandy, 3 of brown sugar, 1 of tartar, and $\frac{1}{2}$ of sour dough, if left for some weeks in a warm place, yield a strong and pleasant vinegar.

On the large scale, an infusion of malt, which has previously undergone the vinous fermentation, is mixed with a little sour dough or other ferment, and left in a warm chamber with free access of air, till the acetification is complete.

In wine countries, inferior wines, which have already become somewhat sour, are employed. The wine is mixed with a little vinegar, and exposed to the air in casks, partly filled with the pressed husks of the grapes. From time to time the liquid is drawn off below, air supplies its place, and the husks become warm by absorbing oxygen, which they yield to the alcohol when it is again poured into the vessel. By repeating this process the acetification goes on rapidly. The addition of more or less brandy enables the manufacturer to procure vinegar of any desired strength.

By attending strictly to all the circumstances, such as temperature, free access of air, exposing a large surface of liquid, &c. which favour the oxidation of alcohol, the time necessary to produce vinegar may be greatly curtailed. This is done in the improved method of acetification. In this, the liquid to be acetified, namely, 1 part alcohol at 80 p. c., 4 to 6 parts of water, and $\frac{1}{1000}$ of ferment, honey, or extract of malt, is made to trickle down through a mass of shavings steeped in vinegar. By this means the surface exposed to the air is prodigiously increased. The liquid is first warmed to between 75° and 83°; but the temperature quickly rises to 100° or 104°, and remains stationary at that point while the action goes on favourably. When the liquid has been three or four times passed through the cask with shavings, it is found to be completely acetified. This requires from 24 to 36 hours. All fermented liquors may be acetified in this way. Should the supply of air be deficient, the alcohol is not entirely acetified, part of it remaining in the state of aldehyde, which, being volatile, flies off and causes a corresponding loss of acetic acid (see p. 864). In some manufactories, great loss was sustained from this cause; which Liebig, after his discovery of aldehyde, was enabled to detect, and completely to obviate. The presence of essential oils, or the smallest trace of pyroligneous acid (see below), prevents the acetification of alcohol.

An ounce of good vinegar ought to saturate 30 to 32 grains of pure and dry carbonate of potash. Such vinegar contains about 5 p. c. anhydrous acetic acid. Its sp. g. is 1·01 to 1·03.

The adulteration of vinegar with sulphuric or hydrochloric acid is detected by nitrate of baryta or of silver; but it must be borne in mind that most vinegars contain naturally a trace of sulphates.

Vinegar also contains tartaric acid, which precipitates with baryta and silver; but the precipitates are soluble in nitric acid.

The pleasant refreshing odour of good vinegar is derived from acetic ether. There are wine vinegars, beer vinegars, and malt vinegars, which, besides acetic ether, contain respectively all the foreign matters of the wine, beer, or infusion of malt. All of them yield by distillation a purer and somewhat weaker acid, *distilled vinegar*. The vinegar made from brandy by the process above-described is as pure as distilled vinegar.

Pyroligneous Acid; Wood Vinegar.—By the dry distillation of wood this vinegar is obtained, at first charged with the oil of tar, from which it is freed by rectification, and by neutralization with soda. The impure acetate of soda is purified as will be hereafter described, and decomposed by sulphuric acid, when a colourless acetic acid is obtained, much stronger than distilled vinegar. It is reduced with water, but of course has not the same flavour as those vinegars which contain acetic ether, &c. The impure pyroligneous acid contains many products of destructive distillation; among others, creosote, which communicates to it a high degree of antiseptic power. Meat preserved by it acquires from the creosote a very agreeable smoked flavour.

PURE HYDRATED ACETIC ACID.

Prep.—1. Three parts of dry, finely powdered acetate of soda (from pyroligneous acid) are mixed, in a capacious retort, with 9·7 parts of purified oil of vitriol. Sufficient heat is developed by the action to cause $\frac{1}{8}$ of the acetic acid to distil over without fire. Heat is then applied till the mass in the retort becomes entirely liquid. The product is rectified, and yields 2 parts of very pure acid, containing 20 p. c. water. The later portions that distil over, exposed in a close vessel to a temperature below 40°, deposit crystals of hydrated acetic acid: the liquid portion, which is somewhat weaker, being poured off, the crystals are melted, and again crystallized by cooling. When the liquid this time is poured off, the hydrate may be considered pure.—2. Three parts of dried acetate of lead are distilled with 8 parts of oil of vitriol, and the product treated as above. If it contain sulphurous acid, this is removed by agitating with peroxide of lead before rectifying. Acid containing 20 p. c. of water, yields a good deal of its superfluous water to dry sulphate of soda. If poured off from the salt, and then rectified, it yields a large proportion of the crystallizable hydrate.

Prop.—Hydrated acetic acid crystallizes at temperatures below 62° in colourless, transparent, brilliant, broad scales and tables; fusible at 62°, forming a liquid of sp. g. 1·063, of a very penetrating, peculiar, and agreeable odour, and a most pungent acid taste. It acts strongly on the skin, causing redness and blistering. It boils at about 248°, fumes slightly in a moist atmosphere, and attracts moisture from it. It is miscible in all proportions with water, alcohol, and ether, also with essential oils; and it dissolves camphor and various resins. Its vapour is inflammable. Sulphuric acid added to it, causes heat and blackening, with disengagement of sulphurous acid gas. Nitric acid exerts no peculiar action on it. It is not decomposed by chlorine in the dark, and when cold; but, with the aid of the sun's rays, the chlorine removes part of the hydrogen as hydrochloric acid, while the hydrogen is replaced by another portion of chlorine, forming a new acid, *chloracetic acid.* The vapour of acetic acid, passed through a tube at a low red heat, is resolved into carbonic acid and acetone; at a higher temperature it produces inflammable gases with deposition of carbon.

Formula of hydrated acetic acid, $C_4H_3O_3 + HO$.

When hydrated acetic acid is mixed with a certain proportion of water, condensation takes place, and the sp. g. of the diluted acid is greater than that of the concentrated. When equal weights are employed, the resulting acid has the same sp. g. as the pure hydrate. A mixture of 77·2 hydrated acid, and 22·8 water, has the highest sp. g. = 1·079. It boils at 220°. This acid contains exactly 3 at. water to 1 at. anhydrous acid. It is obvious that the sp. g. is no test of the strength of the acid, since within certain limits the same sp. g. belongs to acid of two different strengths. This phenomenon does not occur in other acids, in all of which the sp. g. diminishes in proportion to the water which is added, while in the acetic acid it increases up to the point above-mentioned, and beyond that again diminishes, with the addition of water.

The hydrated acid, holding camphor and essential oils in solution, constitutes the aromatic vinegar of the shops, which is used as a stimulus against fainting, and externally as a rubefacient. Common and distilled vinegar are used in pharmacy for preparing many remedies, and externally in medicine in the form of lotions. The use of vinegar as a condiment is universal. It is likewise the antiseptic ingredient in pickles. The raw pyroligneous acid is, however, a far more powerful antiseptic than ordinary vinegar, owing to the creosote it contains, which gives a smoked flavour to meat preserved by means of it. The purity of vinegar or acetic acid is easily ascertained. When diluted, it should give no precipitate with salts of baryta or silver; and when boiled with solution of indigo, it ought not to change the colour. Nitric acid, if present, would give to the indigo a yellow colour.

ACETIC ACID AND BASES.

Acetic acid forms, with ammonia and metallic oxides, soluble salts. The acetates of silver and protoxide of mercury are sparingly soluble. The oxygen of the base is to that of the acid, in the neutral acetates, as 1 to 3. Acetic acid forms also basic salts, with 1½ and 3 times as much base as in the neutral acetates. The fixed alkaline acetates and those of the alkaline earths, when exposed to heat in close vessels, yield water and acetone, (see acetone,) and leave a residue of the carbonate of the base. Other acetates yield a mixture of acetic acid and acetone; while the metallic oxide, or sometimes even the reduced metal, is left. The solutions of the alkaline acetates become mouldy when kept.

All acetates, when oil of vitriol is poured on them, give off vapours of acetic acid, easily recognized by its smell. The acetates of potash and soda may be mixed with the salts of peroxide of iron, oxide of chromium, and peroxide of tin, without precipitation; but, if the mixture be heated, these oxides are entirely precipitated as basic salts, which, if left in the solution, are redissolved on cooling.

Acetate of Oxide of Ethule. Syn. Acetic Ether.—*Prep.* Sixteen parts of dry acetate of lead, 4½ of alcohol, and 6 of oil of vitriol; or 10 parts of crystallized acetate of soda, 15 of oil of vitriol, and 6 of alcohol at 80 to 85 p. c., are distilled together. The product is rectified with slaked lime and chloride of calcium, to remove acid and water, and a quantity of acetic ether equal in weight to the alcohol is obtained. It may also be obtained by distilling hydrated acetic acid with sulphovinate of potash.

Prop.—A colourless liquid, inflammable, and burning with a yellow flame; of a very agreeable, refreshing odour; boiling at 165°, sp. g. 0·89 at 60°; neutral to test paper; soluble in 7 parts of water, in alcohol and ether in every proportion. It is very easily decomposed by alkalies. Oil of vitriol resolves it into ether and acetic acid.

Formula, $C_4H_5O + C_4H_3O_3$, or $AeO + \bar{A}$.

Acetic ether enters into the composition of various remedies in use on the Continent. As a solvent, its properties resemble those of ether, and it might probably be employed advantageously in the preparation of varnishes, from its power of dissolving resins and essential oils.

Acetate of Ammonia.—When equal weights of sal-ammoniac and acetate of potash are distilled together, ammonia is expelled, and binacetate of ammonia distils over as an oily liquid, which on cooling forms a radiated mass of transparent needles, which is deliquescent, and soluble in alcohol. By passing dry ammonia into the melted binacetate, it becomes solid, and is converted into neutral acetate, which forms a white inodorous mass, very soluble in water and alcohōl, resolved by heat into ammonia and binacetate.

Formula, $NH_3,HO,C_4H_3O_3$, or $(NH_4)\ O + \bar{A}$.

A diluted solution of this salt is much used as a diaphoretic in febrile diseases, under the name of Liquor acetatis ammoniæ, formerly Spirit of Mindererus. It is generally made by exactly neutralizing distilled vinegar with carbonate of ammonia. As distilled vinegar, however, varies much in strength, a better formula is to neutralize 6 parts of aqua ammoniæ, sp. g. 0·96, with strong acetic acid, and to add as much water as makes up 24 parts. This solution is somewhat stronger than that of the British pharmacopœias; but it is uniform, and can easily be reduced.

Acetate of Potash.—Prepared by saturating pure vinegar with carbonate of potash, and evaporating to dryness, taking care always to have a slight excess of acid present, without which the salt turns yellow or brown. It crystallizes with difficulty, and is generally obtained in a soft fibrous mass, which feels unctuous to the touch, and has a warm, pungent, sweetish and saline taste. It deliquesces in the atmosphere, and must be kept in closely stoppered bottles. It is soluble in alcohol, and the solution is decomposed by a current of carbonic acid gas; bicarbonate of potash is deposited, and acetic ether is formed. The aqueous solution of acetate of potash absorbs chlorine, and acquires powerful bleaching properties. The dry salt, distilled with arsenious acid, yields alkarsine. Acetate of potash exists in the juice of many plants, and when they are incinerated passes into carbonate of potash. Acetate of potash is a powerful diuretic, and is frequently used in medicine.

Formula, $KO + \bar{A}$.

Acetate of Soda.—Prepared on the small scale as the preceding salt. Or by precipitating acetate of lead with an excess of carbonate of soda, neutralizing the filtered liquid with acetic acid, evaporating to the consistence of syrup, and allowing it to cool slowly. (Acetate of potash may also be prepared in this way.) On the large scale, acetate of soda is prepared from the raw pyroligneous acid, for the purpose of yielding pure acetic acid. The following is an outline of the process. The raw acid is rectified, neutralized with chalk and milk of lime; and, when the solution of acetate of lime is concentrated and hot, sulphate of soda is added. A double salt of sulphate of soda and sulphate of lime is precipitated, and the filtered liquid contains acetate of soda. It is more economical to neutralize the raw acid directly by sulphuret of sodium. Any trace of lime is removed by a little carbonate of soda; and the liquid is evaporated in leaden vessels till it has the sp. g. 1·356, and then put to crystallize in earthenware pans. The crystals which are deposited, and which are impure, are next melted in an iron pot at a moderate heat, and roasted as long as empyreumatic oil comes off. The black carbonaceous residue is digested with cold water, and the filtered liquid is evaporated for a second crystallization. The salt thus obtained serves for the preparation of the commercial pyroligneous acid, of sufficient purity to be used as vinegar when reduced with water. If it be required to prepare perfectly pure acid, the acetate of soda must be subjected to a second fusion and a third crystallization, when it is obtained snow-white. To prepare the wood vinegar of commerce, which generally requires seven waters to reduce it to the strength of ordinary vinegar, 10 parts of acetate of soda, once fused, in crystals, are distilled with 6 parts of oil of vitriol.

Prop.—Acetate of soda, by slow evaporation, crystallizes in transparent, oblique, rhombic prisms, of a pleasant cooling saline taste. Is soluble in 3 parts water at 60°, in 5 parts alcohol; effloresces in a dry air; when heated, melts first in its water of crystallization, frothing much; in a higher temperature the dry salt again melts, and bears a low red heat without decomposition. The melted salt, on cooling, splits with a loud noise in all directions. If deliquescent, it is contaminated with acetate of potash.

Formula, $NaO + \bar{A} + 6\,aq$.

Acetate of Baryta.—Prepared by dissolving carbonate of baryta or sulphuret of barium in acetic acid, and evaporating the filtered liquid. It forms large, transparent, oblique, rhombic prisms, or irregular eight-sided prisms, very soluble, when allowed to evaporate spontaneously. These crystals contain 3 at. water, and are efflorescent. When evaporated at temperatures above 60°, the crystals contain only 1 at. water. Formula, $BaO + \bar{A} + aq$. It is used in analysis to precipitate sulphuric acid, where it is desirable not to introduce nitric or muriatic acid.

Acetate of Strontia.—Crystallized above 60°, contains 1 at. water to 2 at. dry salt; by spontaneous evaporation it yields crystals with 4 at. water, which are efflorescent.

Formula, $SrO\bar{A} + \frac{1}{2}$ aq.

Acetate of Lime is obtained from pyroligneous acid, as above described. Crystallizes in silky needles of an astringent, bitter, and saline taste. Effloresces at 212°; and if heated to 226°, and triturated in the dark, it phosphoresces strongly. Is used for the preparation of acetic acid, acetate of soda, and acetates of lead and copper, &c. from pyroligneous acid.

Formula, $CaO + \bar{A} + aq$.

Acetate of Magnesia.—A very soluble, bitter salt, which crystallizes with difficulty.

Formula, $MgO + \bar{A}$.

Acetate of Alumina.—Prepared by precipitating acetate of baryta with sulphate of alumina. It is uncrystallizable, and dries into a gummy mass, very soluble in water, of a very astringent taste. Heat resolves it into acetic acid and an insoluble basic salt of alumina. The solution may be boiled without decomposition, but possesses the valuable property of depositing when heated a quantity of an insoluble basic salt, if previously mixed with a neutral salt of a mineral acid. Such a mixture, if concentrated, forms, when heated, a gelatinous paste, which disappears on cooling. These properties give to the acetate of alumina a high value in the art of dyeing, as it serves to give to the cloth, by means of the alumina it deposits on it, the power of combining with colouring matter, for which alumina has a remarkable affinity. Such a substance is called a mordant. That commonly used is made by mixing solutions of alum and acetate of lead, in such proportions that all the sulphate of potash of the alum remains undecomposed (100 alum to 120 sugar of lead). The liquor is thickened and stamped on the parts which it is wished to impregnate with the mordant. The cloth is then heated, the acetic acid flies off, and the aluminous precipitate adheres so firmly to the cloth that it cannot be washed away. If the cloth be now immersed in a coloured bath, the colour adheres only to those parts on which the mordant was stamped. If a piece of cloth be heated in a diluted solution of the mordant, and then washed, and immersed in the colour, it will be dyed all over, every part being impregnated with alumina.

Formula, $Al_2O_3 + 3\overline{A}$.

Acetate of Manganese.—Prepared by adding pure sulphate of manganese to acetate of lime. It is soluble and crystallizable, and is used in dyeing. It is printed on the cloth, and, when passed through a bath of chloride of lime, a rich brown oxide of manganese is deposited on the cloth.

Formula, $MnO + \overline{A}$.

Acetate of Zinc.—Prepared by dissolving zinc or oxide of zinc in acetic acid. It crystallizes in flexible, brilliant, tabular crystals of a pearly talc-like lustre. By spontaneous evaporation it forms a beautiful dendritic efflorescence. It is, unlike the other salts of zinc, completely precipitated by sulphuretted hydrogen, if neutral. It is used in medicine for the same purposes as the sulphate, and in pharmacy for preparing cyanide of zinc.

Formula, $ZnO + \overline{A} + 3$ aq.

Acetate of Protoxide of Iron.—Prepared by dissolving iron in acetic acid, or by mixing green vitriol with acetate of lead. Should any peroxide be present, it may be reduced to protoxide by sulphuretted hydrogen, a little free acid being previously added. It crystallizes in small needles, which are very soluble in water, and attract oxygen rapidly from the air. It forms, when dissolved in alcohol, the tinctura acetatis ferri, not now much employed. It is used as a mordant in dyeing.

Formula, $FeO, + \overline{A}$.

Acetate of Peroxide of Iron.—Prepared by dissolving well-washed hydrated peroxide of iron in acetic acid, or by precipitating acetate of baryta with persulphate of iron. It does not crystallize; and like acetate of alumina, when heated with neutral salts, deposits an insoluble basic salt of peroxide. Hence it is much used as a mordant, having the great advantage that the acid does not corrode or injure the cloth. It also enters into the composition of some obsolete remedies.

Formula, $Fe_2O_3 + 3\overline{A}$.

Acetate of Cobalt is red in solution, blue when dry. Mixed with common salt, it forms a good sympathetic ink. The characters are hardly visible till heated, when they become green.

Acetate of Nickel.—Green crystals, soluble in 6 parts of water. Both this and the preceding salt are completely precipitated by sulphuretted hydrogen when neutral, but not if free acetic acid be present.

Acetate of Lead. 1. *Neutral.* Syn. Saccharum Saturni; Sugar of Lead.—This well-known salt is prepared either by dissolving litharge (protoxide of lead) in acetic acid, or by the action of acetic acid on metallic lead with the aid of heat. When prepared with litharge, it contains copper, which may be completely separated by digesting the solution with a little metallic lead. It is then evaporated to crystallize, with the addition of a little free acid. When it is to be made with metallic lead, the lead in thin leaves is exposed, half immersed in the acetic acid, to heat and air. In these circumstances it is very rapidly oxidized, and the oxide is dissolved by the acid. Sugar of lead crystallizes in transparent right rhombic-prisms, or in needles. It has a sweetish metallic taste, and is astringent. It is poisonous, chiefly from its tendency to pass into carbonate. When gently heated, it loses water of crystallization, and becomes anhydrous; it is very apt to melt in the earlier stages of the drying, which impedes the operation. The dry salt, more strongly heated, yields much acetone; and leaves a finely divided mixture of carbon and metallic lead, which is a pyrophorus. Sugar of lead is soluble in 1½ parts of water at 60°, and in 8 of alcohol. Aqua ammoniæ does not precipitate the aqueous solution in the cold, but produces a basic salt; if boiled with it, oxide of lead is precipitated in a crystalline form.

Formula, $PbO,\bar{A} + 3\ aq$.

Acetate of lead is much used as an astringent and styptic in diarrhœa, dysentery, and hemorrhages. It may be safely given in large quantity if vinegar be taken along with it to prevent the formation of carbonate, which is the really poisonous compound.

2. *Sesquibasic Acetate of Lead.*—Dry neutral acetate of lead is fused by a moderate heat, until the liquid mass spontaneously forms a white porous mass, which is dissolved in water; the solution evaporated to the consistence of syrup, and set aside. It forms pearly six-sided scales in concentric groups, permanent in the air and in vacuo, very soluble in water and alcohol, alkaline to test paper.

Formula, $3PbO + 2\bar{A}$.

3. *Trisacetate of Lead.* Syn. Subacetate of Lead.—A cold saturated solution of neutral acetate is mixed with one-fifth of its volume of aqua ammoniæ and set aside, when the trisacetate is de-

posited in long needles, which are anhydrous and soluble in water. Or, to obtain it in solution, 7 parts of litharge are digested, with frequent agitation, with a solution of 6 parts of sugar of lead in 30 of water, till the oxide which remains undissolved has become quite white.

The solution, evaporated in a retort, to exclude carbonic acid, which it rapidly absorbs, forms a white opaque mass, consisting of minute needles, very soluble in water. The liquor plumbi subacetatis of the pharmacopœias is a solution of this salt, generally containing some neutral acetate. It is much used as a lotion, and has long been known as Goulard's extract, or Goulard's water. It has a strong alkaline reaction, and absorbs carbonic acid from the atmosphere, becoming turbid from the deposition of carbonate. For this reason it is far more poisonous than the sugar of lead, as it has a much greater tendency to form the very poisonous carbonate. It precipitates solution of gum, and is used as a test for that substance. It yields precipitates with almost all organic acids, even those which are not precipitated by the neutral acetate. It further precipitates albumen, caseous matter, and extractive matter, and is much employed to remove such substances from organic mixtures.

Formula, $3PbO + \overline{A}$.

4. *Sexbasic Acetate of Lead.*—Prepared by adding the solution of the preceding salts to an excess of ammonia. It forms a white precipitate, composed of minute crystals, slightly soluble in hot water, from which it crystallizes on cooling. White lead is commonly a mixture of this salt with carbonate of lead.

Formula, $6PbO + \overline{A}$.

Acetate of Copper. 1. *Neutral.*—Prepared by dissolving verdigris (see below) in acetic acid with the aid of heat, and crystallizing. It appears in two forms: in dark green, oblique, rhomboidal prisms, which gradually become opaque in the air; formula, $CuO, \overline{A} + aq.$: and in oblique four-sided prisms, of a beautiful blue colour, which form when the solution crystallizes at temperatures below 46°; Formula, $CuO,\overline{A} + 5$ aq. The latter crystals, when heated to 86°, split up into small crystals of the former variety, giving off 4 at. water. Acetate of copper, heated in the air, burns with a lively green flame. If heated in close vessels, it gives off acetic acid and acetone, and leaves finely divided metallic copper, which is easily inflammable. The solution, boiled with sugar or honey, deposits minute octohedral crystals of suboxide of copper.

Diacetate of Copper. Syn. Verdigris; Ærugo.—It is prepared by exposing plates of copper to the vapours of acetic acid in a warm situation. The verdigris forms on the surface of the copper, and is scraped off from time to time. It forms a bluish-green or green powder, which is resolved by cold water into soluble sesquibasic acetate and insoluble tribasic acetate or trisacetate of copper. It is chiefly used as a pigment, or in the preparation of other pigments, as Schweinfurt or Vienna green.

Formula, $2CuO,\bar{A} + 6$ aq., or $(CuO,\bar{A}$, 5 aq. $+ CuO$, aq.)

Sesquibasic Acetate of Copper.—Is dissolved out of verdigris by water, and forms, when dry, a blue amorphous mass, easily soluble in hot water. It exists in considerable quantity in the blue varieties of verdigris.

Formula, $3CuO,2\bar{A} + 6$ aq.

Trisacetate of Copper.—A green insoluble powder, left undissolved when verdigris is acted on by water. Is the principal ingredient of verdigris, especially the green variety.

Formula, $3CuO,\bar{A}$, 3 aq.

By boiling any of the preceding basic salts for a long time with water, there is left a liver-brown powder nearly insoluble, which is an acetate with a still greater proportion of base. It contains 92 p. c. oxide of copper, according to Berzelius.

Schweinfurt or Vienna Green.—When boiling solutions of equal weights of neutral acetate of copper and arsenious acid are mixed, the mixture added to its own volume of cold water, and the whole allowed to stand for some days, a beautiful green powder is obtained, which is much prized as a pigment, under the above name. When boiled with caustic potash, it leaves suboxide of copper, while arsenic acid is formed.

Acetate of Protoxide of Mercury.—Prepared by mixing hot solutions of protonitrate of mercury and acetate of potash. It is deposited on cooling in white silvery scales, which must be washed with a little cold water, and dried by pressure in bibulous paper in a dark place, as it is decomposed by the light.

Formula, $HgO,\bar{A}$.

It is a pharmaceutical preparation, and occasionally used in medicine.

Acetate of Peroxide of Mercury.—Prepared by dissolving red oxide of mercury in acetic acid, and evaporating. It forms white scaly crystals, soluble in 4 parts of water, decomposed by boiling water.

Formula, $HgO_2,\bar{A}$.

It is now rarely used; but, along with the preceding salt, entered into the composition of Keyser's pills, once a celebrated remedy on the Continent.

Acetate of Silver.—Obtained by dissolving oxide of silver in acetic acid; or by mixing hot saturated solutions of nitrate of silver and acetate of potash. It is sparingly soluble, and crystallizes, on cooling, in pearly, flexible needles. When heated, acetic acid is given off, and pure silver is left. It is used as a test for hydrochloric acid, particularly in testing the purity of acetates.

Formula, $AgO,\bar{A}$.

PRODUCTS OF THE DECOMPOSITION OF ETHER AND ITS COMPOUNDS BY CHLORINE.

The changes which are produced in oxide of ethule by the action of chlorine have lately been carefully studied by Malaguti and Regnault, and the facts discovered by them shed light on a multitude of phenomena, the explanation of which had long been sought for in vain. In treating of the production of acetic acid from alcohol, it has been mentioned that by the action of oxygen 2 eq. hydrogen are removed, and replaced by 2 eq. oxygen. The same reaction takes place with chlorine, and a compound is produced, the formula of which is $C_4H_3\left.\begin{matrix}O\\Cl_2\end{matrix}\right\}$. This formula represents anhydrous acetic acid in which 2 eq. oxygen have been replaced by 2 eq. chlorine. When anhydrous ether is saturated with dry chlorine gas, at first with the aid of external cold, afterwards at a gentle heat, a large quantity of hydrochloric acid gas is disengaged, and there is left a colourless oily liquid, which is the above compound, although not quite pure. It may be called *oxychloride of acetule.* It is contaminated by the presence of a little chloral, and another compound containing chlorine, which seems to be resolved by contact with water into hydrochloric acid and aldehyde. It is kept for some days in contact with water, which is frequently changed, and at last dried in vacuo over sulphuric acid. By these means the pure oxychloride of acetule alone is left. It forms a neutral, heavy, colourless oily fluid, of a penetrating odour, like that of oil of fennel. At 284° it boils and is decomposed. Its characteristic property is that of being converted when warmed with water into hydrochloric and acetic acids. This change is instantaneous in contact with alkaline solutions. Sulphuric acid decomposes and blackens it. When heated with potassium, it yields chloride of potassium and a gaseous compound C_4H_3OCl, containing only half as much chlorine as the original liquid. Compounds of an analogous nature, in which the chlorine is wholly or partially replaced by sulphur, may be obtained by the action of sulphuretted hydrogen gas on the oxychloride. When that gas is passed through the liquid, hydrochloric acid is disengaged, and there is formed an oily, colourless, fetid liquid, which blackens on exposure to the air, and gradually passes for the most part into a crystalline mass. Hot alcohol dissolves this; and on cooling deposits tolerably large colourless prisms, fusible between 228° and 235°, not volatile, insoluble in water, soluble in alcohol and ether. The formula of this compound, which may be called oxysulphuret of acetule, is $C_4H_3\left.\begin{matrix}O\\S_2\end{matrix}\right\}$, according to which it is anhydrous acetic acid in which 2 eq. oxygen have been replaced by 2 eq. sulphur. In contact with an alcoholic solution of potash, it forms sulphuret of potassium and acetate of potash. The mother-liquid of these crystals, on further evaporation, yields yellow unctuous scales, fusible about 160°, and possessing analogous properties. It is distinguished from the first by containing only 1 at. sulphur, and in the place of the second 1 at. chlorine. Its formula is $C_4H_3\left.\begin{matrix}O\\Cl\\S\end{matrix}\right\}$. With an alcoholic solution of potash, this body gives sulphuret and chloride of potassium, with acetate of potash.

The compounds of oxide of ethule (ether) with acids are acted on by chlorine very much as the ether itself; with this difference, that the acids, when not altered by chlorine, and, when they are altered by it, the new substances formed, remain in combination with the oxychloride of acetule.

Oxalic ether is not acted on by chlorine. Acetic ether gives with it a compound, the formula of which is $C_8H_6O_4Cl_2$. It consists of anhydrous acetic acid and oxychloride of acetule, $= C_4H_3O_3 + C_4H_3\left.\begin{matrix}O\\Cl_2\end{matrix}\right\}$. Benzoic ether, when acted on by chlorine, takes up 3 eq. but gives off only 2 eq. hydrochloric acid; and a substance is formed consisting of 1 at. chloride of benzule, and 1 at. oxychloride of acetule. $BzCl + C_4H_3\left.\begin{matrix}O\\Cl_2\end{matrix}\right\}$. Here the chloride of benzule has obviously been formed by the action of 1 eq. hydrochloric acid on 1 eq. anhydrous benzoic acid in the nascent state.

When ether is exposed still longer to the action of chlorine, with a gradually increasing temperature, a heavy oily liquid is at last obtained, which is not acted on by water or aqua potassæ. It may be distilled unaltered with oil of vitriol, at least in great part. It boils at 277°, and has the sp. g. 1·611. In an alcoholic solution of potash it dissolves, chloride of potassium is deposited in abundance, and water separates from the liquid a new oily compound.

If chloride of ethule be exposed in a proper apparatus to the action of chlorine gas and the rays of the sun, a violent reaction takes place, with disengagement of hydrochloric acid. A new compound is formed, which has the same composition, and the same density in the state of vapour, as the so-called oil of olefiant gas. Its smell and some other properties are also very similar, but it is in reality a very different body. It boils at 149°, and may be distilled with potassium or an alcoholic solution of potash without change. Its formula is $C_4H_4Cl_2$, so that it is derived from chloride of ethule, C_5H_5Cl, in which 1 eq. hydrogen is replaced by 1 eq. chlorine.

When this compound is exposed to the further action of chlorine and light, a series of remarkable compounds is obtained. The first is a compound of chlorine, analogous to acetic acid, in which all the oxygen is replaced by its equivalent of chlorine.

Formula, $C_4H_3Cl_3$.

It may be called *Chloride of Acetule.* It boils at 167°. The sp. g. of its vapour is 4·61. The formula of the next compound is $C_4H_2Cl_4$. It boils at 215°. Its sp. g. as vapour is 5·79. A third compound is C_4HCl_5; and the fourth and last is chloride of carbon C_4Cl_6, or $2(C_2Cl_3)$, in which all the hydrogen of ethule is replaced by chlorine. (Regnault.)

CHLORAL.

By the action of chlorine on alcohol *Chloral* is formed; a substance which represents aldehyde in which the hydrogen of the oxide of acetule is replaced by chlorine.

C_4H_3O+HO hydrated oxide of acetule. Aldehyde.
C_4Cl_3O+HO chloral.

Apparently the effect of chlorine on alcohol is first to form aldehyde, and by the further action of the chlorine on that substance the chloral is formed. But the attempts which have been made to form chloral by the direct action of chlorine on aldehyde have failed, owing to the facility with which aldehyde is converted into a number of different products. Chloral is obtained, but mixed with other compounds of chlorine. Very diluted alcohol yields with chlorine only aldehyde and hydrochloric acid; and an excess of chlorine causes the aldehyde to pass into acetic acid. Alcohol of 80 to 85 p. c. yields with chlorine the so-called heavy muriatic ether. To prepare chloral, anhydrous alcohol is placed in a retort, and dry chlorine is passed through it. At first cold must be applied, but afterwards a gentle heat is required to promote the action. Every bubble produces a flash of light, and a very long time is required to complete the decomposition of only a moderate quantity of alcohol. An enormous quantity of hydrochloric acid is disengaged, which must be sent either up the chimney or out of the window. This is best done by introducing through the neck of the retort into the body, a long tube, which is bent upwards after it leaves the retort, and by which the gas may be conducted away. In this tube alcohol and chloral, carried off by the gas, are condensed, and flow back into the retort. The chlorine is introduced by a tube passing through the tubulure of the retort. As soon as chlorine, even at the boiling temperature, passes through unchanged, the operation is complete. The liquid generally solidifies on cooling, forming a white crystalline mass, *hydrate of chloral.* It is melted by a gentle heat, and agitated in a stoppered bottle with twice or thrice its volume of oil of vitriol. When the mixture is gently warmed, impure chloral rises to the surface, as a colourless oily stratum. It is removed, and boiled for some time, to expel hydrochloric acid and alcohol; and distilled with its own volume of oil of vitriol. It is finally rectified along with finely powdered quicklime, and the distillation is stopped as soon as the surface of lime is dry. What has passed over, is pure chloral.

Formula, $C_4Cl_3O + HO$, or $C_4HCl_3O_2$.

Chloral is a mobile oily liquid of a peculiar penetrating, agreeable smell. It causes a flow of tears. Its taste is at first slight and fatty, afterwards acrid. Its sp. g. at 65° is 1·502. It boils at 202°. It is miscible with ether and alcohol, and dissolves sulphur, phosphorus, and iodine. The *hydrate of chloral,* according to Dumas, consists of 1 at. chloral and 2 at. water. When chloral is mixed with water, it at first dissolves, and after some minutes is converted into a semi-solid mass, translucent, and formed of fine needles, soluble in a larger quantity of water, and crystrallizing in large rhomboidal crystals by the evaporation of this solution in vacuo over sulphuric acid. The formation of this hydrate in the preparation of chloral from anhydrous alcohol depends on the action of the hydrochloric acid produced in the process on a portion of undecomposed alcohol, whereby chloride of ethule and water are formed. The solution of chloral has the taste and smell of that substance, is neutral, and does not precipitate nitrate of silver.

The dry hydrate may be distilled without change. When heated with caustic alkalies, it is resolved into perchloride of formule, formiate of the alkali, and chloride of the metal. If to the elements of 1 at. choral,

$C_4H\ Cl_3O_2 = 1$ at. chloral,
We add $H \quad O = 1$ at. water,

The sum $C_4H_2Cl_3O_3$ is equal to
$C_2H\ O_3 = 1$ at. formic acid,
And $C_2H \quad Cl_3 = 1$ at. perchloride of formule.

$C_4H_2O_3Cl_3$.

The metallic chloride, formed along with the alkaline formiate, is a secondary product of the decomposition of the perchloride of formule. The final result appears to be that from 6 at. chloral and 10 at. alkali there are obtained 3 at. metallic chloride, 7 at. alkaline formiate, and 5 at. perchloride of formule.

Chloral, like aldehyde, cannot be kept without change. After some time it solidifies into a white translucent mass like porcelain, the so-called insoluble chloral. This change takes place equally in close vessels and in the air. There is no disengagement of gas and no gain of weight. This solid body is most readily formed, when alcohol charged with chlorine, as in the preparation of chloral, is mixed with oil of vitriol and allowed to stand in open vessels. The oily stratum swimming over, the acid very soon solidifies, and the degree of its solidification furnishes the best test of the progress of the operation. The insoluble chloral appears to be partially decomposed by washing with water. When distilled, it yields chloral, which soon solidifies again. Treated with potash it yields formiate of potash and perchloride of formule, with chloride of potassium, just as chloral does.

From the mode of its formation, it is probable that this substance differs from chloral, exactly as metaldehyde and elaldehyde do from aldehyde. The analyses, however, which have been made of insoluble chloral, indicate a difference between its composition and that of chloral. But this is probably owing to the partial decomposition it had undergone in being washed previous to analysis.

CHLORACETIC ACID.

Discovered by Dumas. Pure hydrated acetic acid is exposed to the combined action of chlorine gas and the sun's rays. After 24 hours the sides of the vessel are covered with crystals, which are dissolved out by a small quantity of water. The solution contains chloracetic acid, with hydrochloric, oxalic, and acetic acids. It is allowed to evaporate in vacuo, over saucers containing oil of vitriol and fused potash. Oxalic acid first crystallizes, then chloracetic acid. The mother-liquid is distilled with anhydrous phosphoric acid, which retains the water, and decomposes the oxalic acid. Acetic acid first passes over, then chloracetic acid in crystals, which are purified by wrapping them in bibulous paper, and leaving them in vacuo for 24 hours. Pure chloracetic acid is left. It forms colourless rhomboidal needles and plates, with a faint smell and a caustic taste, very deliquescent in moist air. It bleaches and corrodes the skin, causing blisters. The vapour of the acid, when heated, is very irritating and suffocating, and very oppressive to the respiratory organs. The solution reddens vegetable blues without bleaching them. The crystals melt at 115°, but do not again become solid till the temperature falls to 108°. The sp. g. of the liquid acid at 115° is 1·617. When heated with an excess of potash, this acid undergoes a very striking change. It is resolved into perchloride of formule and carbonic acid; or we obtain chloride of potassium, formiate of potash, and carbonate of potash.

Formula, $C_4Cl_3O_3 + HO$.

Chloracetic acid combines with bases, its water being replaced by an equivalent of the base; and forms salts which are soluble in water, and possess a remarkable analogy with the acetates. As the acetates are decomposed by digestion with excess of alkali, becoming brown, so also are the chloracetates, only with greater facility.

Chloracetate of Ammonia.—Formula, $C_4Cl_3O_3 + NH_4O + 4$ aq. It is crystallizable; and is decomposed when heated with excess of ammonia, yielding perchloride of formule and carbonate of ammonia. This is easily explained, as the chloracetic acid contains the elements of 1 at. perchloride of formule and 2 at. carbonic acid. $C_4Cl_3HO_4 = C_2HCl_3 + 2CO_2$.

Chloracetate of Oxide of Ethule.—Prepared by distilling a chloracetate, or chloracetic acid, with sulphuric acid and alcohol. Water, added to the product, separates the chloracetic ether in the form of a colourless heavy oil, having an odour similar to that of the so-called heavy muriatic ether.

Formula, $C_4Cl_3O_3,AeO$.

Chloracetate of Potash.—Obtained by neutralizing the acid with carbonate of potash, and spontaneous evaporation of the solution, in fine silky crystals, permanent in dry, but deliquescent in moist air. When heated, is decomposed with a feeble explosion. Boiled with excess of potash, it yields a large quantity of formiate of potash.

Formula, $C_4Cl_3O_3,KO + aq$.

Chloracetate of Silver.—Prepared by dissolving oxide of silver in the acid, and evaporation in vacuo. It forms shining scales or crystalline grains. It is sparingly soluble in water, and explodes when heated. If moistened with alcohol, and set fire to, chloride of silver is left.

Formula, $C_4Cl_3O_3,AgO$.

HEAVY MURIATIC ETHER.

This name has been given to a liquid obtained by Scheele from the distillation of oil of vitriol, chloride of sodium, hyperoxide of manganese, and alcohol; and which is also obtained when alcohol of 80 to 85 p. c. is saturated in the cold with chlorine, then mixed with water, and the oily fluid which separates washed with water as long as any of it is dissolved. These products, which vary much in composition, enter into the constitution of the spiritus muriatico-ethereus, a remedy occasionally used on the Continent. A similar substance is obtained by saturating alcohol with chloride of lime, mixing it with twice its volume of water and distilling it, without separating the oil which is deposited, along with half its weight of hyperoxide of manganese. The product, well washed with water, is the pure ether in question. It boils at from 230° to 250°. Its sp. g. is 1·227. Heated with aqua potassæ it is decomposed, with disengagement of heat; and a new liquid containing chlorine distils over, which boils at 219°, and has the sp. g. 1·074. The potash retains a brown resinous matter. The heavy muriatic ether, as first obtained, contains oxychloride of acetule, and a substance which, by the action of water, is converted into aldehyde and hydrochloric acid; but its composition in the pure state is not known, and the whole subject requires a thorough investigation.

BROMAL.

Discovered by Löwig. Formula, $C_4Br_3O + HO$. It is obtained by the action of bromine on alcohol, and is purified much in the same way as chloral, to which it is quite analogous. It is a colourless oily fluid, of a penetrating odour, which attacks the eyes. It boils above 212°. Sp. g. 3·34. With caustic alkalies it undergoes the same change as chloral, producing bromide of the metal, perbromide of formule, and formiate of the alkali. Bromal forms a hydrate with 4 at. water, which readily crystallizes. When bromine is made to act on ether, a variety of compounds is produced, the nature of which has not yet been ascertained.

IODINE AND ALCOHOL.

Iodine is soluble in alcohol, forming a deep brown solution. If this be mixed with an alcoholic solution of potash, it yields iodide of potassium, formiate of potash, and iodide of formule, in silky yellow crystals. If iodine and alcohol be added to strong nitric acid, as long as the liquid remains colourless, an oily liquid is obtained according to Johnston, the composition of which is unknown. According to Aimé, if 4 parts of alcohol and 1 of iodine be mixed, and 1 part of fuming nitric acid added, the mixture, being left to itself deposits an oily liquid, of which likewise nothing certain is known.

Chlorocyan-aldehyde.— Formula, $C_{16}H_{14}O_8N_4Cl_4$. If a current of dry chlorine be passed through a solution of bicyanuret of mercury in alcohol, kept as cool as possible, an immense number of crystals make their appearance in the liquid. These consist of a mixture of sal-ammoniac and the aldehyde compound. The crystals are to be thrown upon a filter and washed with cold water, till every trace of sal-ammoniac and cyanuret of mercury is removed. By dissolving them again in alcohol much larger crystals may be obtained. They have a silvery lustre, resembling sulphate of quinine, are neutral, have neither taste or smell. They melt at 120°, but are partly sublimed before melting. They are insoluble in cold water, but very soluble in alcohol and ether.—Steinhouse.

The above empirical formula may be represented as follows: $3(C_4H_4O_2) + 2CyCl + 2HO$; that is, 3 at. aldehyde, 2 at. chloride of cyanogen, and 2 at. water.

The chlorocyanic ether of Aimé is no determinate compound, but consists chiefly of a mixture of light and heavy muriatic ether.

PRODUCTS OF THE DECOMPOSITION OF ALCOHOL, THE CONSTITUTION OF WHICH IS UNCERTAIN.

Under the name of olefiant gas, a substance has been frequently mentioned in the preceding pages, which is produced as a constant result of the decomposition of alcohol by an excess of sulphuric acid. This substance consists of carbon and hydrogen, equivalent to equivalent. It is distinguished from all other carbo-hydrogens by its tendency to combine as well with simple as with compound bodies. It is named from the fact of its forming an oily compound with chlorine. Berzelius calls it Elayle. But if we examine closely its chemical relations, it appears highly probable that the formula $C_4H_3 + H = C_4H_4$ represents its constitution. This view sheds much light over the cause of its tendency to enter into new combinations, and the phenomena attending the decomposition of its compounds. According to this formula, it is a hyduret of acetule, corresponding to the oxide of acetule.

It is obtained in a state of purity, when 1 part of alcohol is heated with 6 or 7 of oil of vitriol. At first ether, then oil of wine, passes over; at last there comes a mixture of equal volumes of sulphurous acid and olefiant gas. It is purified by passing it through milk of lime, which retains the sulphurous acid, and through oil of vitriol, which absorbs water, ether, and alcohol. Pure hyduret of acetule has a feeble ethereal odour; it burns with a white and very luminous flame. In contact with chlorine, equal volumes of the two gases condense into an oily fluid, the hydrochlorate of chloride of acetule, or the oil of the Dutch chemists. Olefiant gas combines with bromine, iodine, and anhydrous sulphuric acid. When 1 vol. of this gas and two vol. chlorine are quickly mixed in an open cylinder, and a burning body approached to the mixture, combustion takes place with a red flame, without explosion; hydrochloric acid is formed, and carbon is deposited in thick flocculi.

Chloride of Acetule. — When the oil above-mentioned (hydrochlorate of chloride of acetule) is left for some days in contact with an alcoholic solution of potash, the hydrochloric acid is destroyed, producing water and chloride of potassium, and there is left protochloride of acetule, which is dissolved by the alcohol. A gentle heat disengages it in the form of gas, along with the vapours of alcohol and water. The gas is purified by being passed through oil of vitriol. Protochloride of acetule is gaseous at the ordinary temperature, has an alliaceous smell, burns with a dark-red flame fringed with green; its sp. g. in the state of gas is 2·166. At 0° it condenses into a liquid. Potassium, heated in the gas, decomposes it, producing chloride of potassium, naphthaline, and carbon.

Formula, C_4H_3Cl.

If this gas be passed through the perchloride of antimony, it is entirely absorbed. The addition of water separates a liquid, which is a mixture of the oil of olefiant gas with another compound, which has the empirical formula $C_4H_3Cl_3$, and might be considered, like the compound mentioned (p. 889), as acetic acid in which the oxygen is replaced by chlorine; but, from the phenomena of its decomposition by potash, its real formula must be $C_4H_2Cl_2 + HCl$. When the above mixture is distilled, the oil of olefiant gas passes over, till the temperature rises to 235°; after which the new compound passes over pure. It is fluid, colourless, of sp. g. 1·422 in the liquid form: in the form of vapour, 4·75. When it is distilled with an alcoholic solution of potash, it produces chloride of potassium, water, and a new substance, boiling at 86°, the formula of which is $C_4H_2Cl_2$. Its density in the form of vapour is 3·34. If we take the half of the above formula, C_2HCl, this substance would seem to be the protochloride of formule, the radical of formic acid. This name has been given to it by Regnault, who discovered it.

Perchloride of Acetule.—This is the compound corresponding to acetic acid, which Regnault obtained by the action of chlorine on the chloride of ethule with the aid of the sun's rays.

Formula, $C_4H_3Cl_3$. (See p. 889.)

Protobromide of Acetule.—Prepared as the proto-chloride, only using the corresponding compound of bromine. It is gaseous, has an alliaceous smell. Its sp. g. in the form of gas is 3·691.

Formula, C_4H_3Br.

Hydrochlorate of Chloride of Acetule. Syn. Oil of Olefiant Gas; Oil of the Dutch Chemists.—Discovered by Deimann, Troostwyk, Lauwerenburgh, and Vrolich. It is commonly prepared by mixing moist chlorine and olefiant gases in equal volumes; but it is preferable to pass olefiant gas into perchloride of antimony as long as it is absorbed. The saturated fluid is distilled, when the oil in question passes over. It is purified by repeated rectification with oil of vitriol, and washing with water, and is dried by means of chloride of calcium.

It is a colourless mobile liquid, of an agreeable ethereal odour and a sweet taste. It boils at 180°. The sp. g. of its vapour is 3·4484. It is not altered by distillation with oil of vitriol or with caustic potash. It burns with a luminous flame edged with green, and smoky. It communicates to water its smell, without being perceptibly dissolved; and it is miscible in all proportions with alcohol and ether. When mixed with an alcoholic solution of potash, it is gradually decomposed, yielding chloride of potassium and protochloride of acetule. It absorbs chlorine, producing hydrochloric acid, and other compounds richer in chlorine. Among these are the compound already mentioned, $C_4H_2Cl_2 + HCl$; and another, $C_4H_2Cl_4$, or $C_2H + Cl_2$, which may be considered as the deutochloride of formule. When all the hydrogen is replaced by chlorine, which happens after long exposure to the combined action of light and chlorine, there is obtained sesquichloride of carbon, $C_4Cl_6 = 2(C_2Cl_3)$.

Under the name of Chloretheral, D'Arcet has described a substance produced by the action of chlorine on impure olefiant gas, containing the vapours of alcohol and ether. When the oil so obtained is rectified till the temperature rises to 365°, this substance then passes over. It is a colourless liquid of a peculiar odour, different from that of the oil of olefiant gas. It is decomposed by water, alkalies, and sulphuric acid. According to D'Arcet, its formula is C_4H_4OCl; so that it may be a compound of

$$\begin{array}{rll}
 & C_4H_3O + HO & = \text{hydrated oxide of acetule. Aldehyde.} \\
\text{and} & C_4H_3Cl + HCl & = \text{hydrochlorate of chloride of acetule.} \\
\hline
 & C_8H_8O_2Cl_2 & = 2(C_4H_4OCl) \\
 & & \text{or of} \\
 & C_4H_3OCl_2 & = \text{oxychloride of acetule,} \\
\text{and} & C_4H_5O & = \text{oxide of ethule.} \\
\hline
 & C_8H_3O_2Cl_2 & = 2(C_4H_4OCl).
\end{array}$$

This substance is worthy of more minute investigation.

Hydrobromate of Bromide of Acetule.—Discovered by Serullas. Prepared by the action of bromine on olefiant gas. In its formation, its purification, and properties, it is very analogous to the corresponding compound of chlorine already described. Sp. g. at 70°, 2·164. It boils at about 265°, and solidifies at 5°.

Formula, $C_4H_3Br + HBr$.

Hydriodate of Iodide of Acetule.—When iodine is exposed to the action of olefiant gas, a solid compound is obtained, heavier than oil of vitriol, fusible at 175°, and forming a crystalline mass on cooling. It is decomposed by chlorine and bromine. It is uncertain, from the weaker affinities of iodine, whether it be really a compound analogous to the two preceding, $C_4H_3I + HI$; or whether its more probable formula be not $(C_4H_3)H + I_2$, that is, a compound of hyduret of acetule (olefiant gas) with iodine.

Hyposulpho-acetylic Acid, or *Quadrisulphate of Hyduret of Acetule.*—Discovered by Regnault. Olefiant gas is absorbed by anhydrous sulphuric acid, with production of heat, and without blackening. The acid ceases to fume on exposure to the air, and is converted into a white crystalline body, which is fusible at 175°, and may be sublimed. When dissolved in water, it takes up 1 at. water, and forms hydrated ethionic acid. (See ethionic acid.) It absorbs ammonia; and, when the compound is gently heated, it is decomposed with explosion, and converted into a black mass. Formula, $4SO_3 + C_4H_3,H$.

Chloride of Platinum and Acetule.—This compound was first noticed by Berzelius, but has been minutely studied by Zeise. It is produced by the action of chloride of platinum on alcohol, along with aldehyde and chloride of ethule. It appears most probable that the oxide of ethule of the alcohol is resolved, as in so many decompositions, into water and hyduret of acetule (olefiant gas); and that the latter, with chloride of platinum, produces the new double chloride, hydrochloric acid, and free chlorine. By the action of the hydrochloric acid on the alcohol, chloride of ethule is formed; and by the action of chlorine on alcohol, aldehyde also is produced. Three at. oxide of ethule, with 4 at. bichloride of platinum, produce 1 at. aldehyde, 1 at. water, 2 at. chloride of platinum and acetule, and 4 at. hydrochloric acid: if this be the true explanation, the formula of the double chloride will be $(C_4H_3)Cl + Pt_2Cl$. It will then correspond to the oil of olefiant gas, $(C_4H_3)Cl + HCl$; one atom of hydrogen being replaced by two of platinum. According to Zeise, the formula is $C_4H_4Pt_2Cl_2$, or $(C_4H_3)H + Pt_2Cl_2$. In this case, 2 at. oxide of ethule with 2 at. bichloride of platinum would form 1 at. of the new compound, 1 at. aldehyde, and 2 at. hydrochloric acid. Malaguti considers the salt in question is a compound of oxide of acetule with chloride of platinum $= (C_4H_3)O + Pt_2Cl_2$. But Zeise's experiments seem to demonstrate the absence of oxygen in the compound; and, besides, it is not easy to see how the chloride of platinum could act on the ether so as to yield Malaguti's formula, along with aldehyde and the other products. On this view 1 at. oxide of ethule should act on 2 at. bichloride of platinum, and the only products should be the double chloride and hydrochloric acid.

The double chloride itself is obtained pure by adding to the solution of the compound it forms with chloride of potassium, or with sal-ammoniac, bichloride of platinum as long as it causes a precipitate, and evaporating the filtered liquid in vacuo over sulphuric acid in a dark place. It forms a transparent honey-yellow mass, which is blackened by light. It is very prone to decomposition. The solution of bichloride of platinum in alcohol always contains a little of this compound. It is soluble in alcohol, and a thin film of this solution, dried on the surface of glass or porcelain, and heated red-hot, leaves a brilliant surface of platinum which adheres very firmly.

The solution of the chloride of platinum and acetule, when digested with hydrate of magnesia, gives chloride of magnesium, which is dissolved, and a slimy greyish brown precipitate, which gradually becomes dense and black. When the excess of magnesia is dissolved out by nitric acid, there remains a black powder, which, if dried and heated, explodes, leaving platinum. It is possible that this may be a compound of acetule with 2 at. suboxide of platinum, or of a compound of platinum and acetule with oxide of platinum. The same substance, although probably containing more platinum, is formed by digesting alcohol with subchloride of platinum. This powder also explodes when heated, and possesses in a high degree the power of absorbing oxygen, converting alcohol into acetic acid, &c.

Triple Chloride of Potassium, Platinum, and Acetule.—Pure bichloride of platinum is dissolved in alcohol with a little hydrochloric acid and one-eighth of its weight of chloride of potassium, and digested at a boiling heat for some time. The alcohol is distilled off, and the residue saturated with carbonate of potash, and evaporated by a gentle heat till it crystallizes. It forms lemon-yellow, regular translucent prisms, which at 212° lose 2 at. water. It is soluble in water, especially if hot; and in alcohol. The solution is decomposed by heat, with the separation of metallic platinum. It is decomposed by the action of light, and of chlorine and hydrogen, when heated in those gases.

Formula, $(C_4H_3)Cl + Pt_2Cl + KCl$.

Similar triple chlorides may be obtained with chloride of sodium and chloride of ammonium (sal-ammoniac). In properties and composition they resemble the salt just described.

When the solution of either of these salts is mixed with ammonia, a lemon-yellow precipitate is obtained, the formula of which is $(C_4H_3)Cl + P_2Cl + NH_3$. It is sparingly soluble in water, soluble in alcohol. It is decomposed by light and heat. Potash disengages ammonia from it.

PRODUCTS OF THE DECOMPOSITION OF ACETIC ACID AND THE ACETATES.

1. *Acetone, its Compounds, and the Products of its Decomposition.*—When the vapour of hydrated acetic acid is passed through a red-hot tube, it is entirely resolved, without deposition of carbon, into a volatile liquid, acetone, and a mixture of carburetted hydrogen, carbonic oxide, and carbonic acid gases. If the heat go beyond a dull red, the acid is resolved into a brown oil and inflammable gases, with deposition of carbon.

Acetates, the bases of which retain carbonic acid at a red heat, produce, when heated in close vessels, the carbonate of the base and acetone. This takes place, for example, with the acetates of potash, soda, and baryta. Where the oxide cannot retain carbonic acid at a red heat, as in the case of acetates of magnesia, zinc, or manganese, the acetone is accompanied by carbonic acid. If the oxide be easily reducible, as in the acetates of copper, silver, and mercury, there are given off hydrated acetic acid, carbonic oxide, carbonic acid, water, and acetone, and there is left a mixture of the metal with carbon in a minute state of division.

Neutral acetate of lead, melted at 365°, solidifies after a time, into a white crystalline frothy mass of sesquibasic acetate of lead, while one-third of the acetic acid is expelled in the form of carbonic acid and acetone. The formula of acetone is C_3H_3O. If to this we add the elements of 1 at. carbonic acid, the result is 1 at. anhydrous acetic acid, $C_3H_3O + CO_2 = C_4H_3O_3$. This explains sufficiently all the above reactions.

Acetone.—The liquid obtained by passing acetic acid through a red-hot tube, or by distilling the acetate of lime, is rectified over quicklime in the water-bath till its boiling point becomes constant. It then forms a clear colourless liquid, of a peculiar, penetrating, somewhat empyreumatic smell. Its sp. g. is 0·7922 in the liquid form; 2·022 in the form of vapour. It boils at 132°. Acetone has a pungent taste, resembling that of peppermint; and is miscible with water, alcohol, and ether in all proportions. In contact with caustic alkalies and air, acetone absorbs oxygen; and produces, among other products not examined, a brown resinous substance. Heated with chloride of lime, it yields carbonic acid and chloride of formule. It is also decomposed by chlorine and oil of vitriol. It is inflammable, and burns with a luminous flame.

Its formula is C_3H_3O.

In the preparation of acetone there is obtained, in variable quantity, an oily liquid, much less volatile than acetone, which remains in the retort when the impure acetone is rectified. It has a disagreeable smell and a burning taste, boils at 248°, the sp. g. of its vapour is 5·204. Its formula is $C_{10}H_8O$. Kane, who described and analysed this oil, has given it the name of Dumasine, out of compliment to M. Dumas. It is to be hoped that this principle of nomenclature may not be followed in chemistry.

The chemical nature and constitution of acetone are still doubtful. It contains the elements of 1 at. carbonate of oxide of ethule and 1 at. hyduret of acetule $= C_9H_9O_3$; or of 1 at. acetate of oxide of ethule and 1 at. hyduret of acetule $= C_{12}H_{12}O_4$. According to Kane, it has a constitution similar to that of alcohol, and is the hydrate of the oxide of an organic radical, $C_6H_5 = (C_6H_5)O + HO = C_6H_6O_2$. This radical he calls *Mesitule.*

By distilling acetone with fuming sulphuric acid, Kane obtained, along with a number of other products, a substance, the formula of which he states to be C_6H_4. (His analysis rather leads to the formula $C_{12}H_9$.) To this substance he has given the name of *Mesitylene.*

By the action of perchloride of phosphorus on acetone, Kane obtained a compound C_6H_5Cl, *chloride of mesitule*, which, by the action of aqua potassæ, yielded chloride of potassium and the compound C_6H_5O, *oxide of mesitule*, differing from acetone as ether does from alcohol, namely, by 1 at. of water. By saturating a mixture of acetone and fuming sulphuric acid with lime and other bases, peculiar salts were obtained, containing the elements of sulphuric acid, oxide of mesitule, and a metallic oxide. These salts, according to Kane, are analogous to the sulphovinates (double sulphates of oxide of ethule and bases); but the theoretical views of Kane concerning these compounds do not appear to express their true nature.

That view which considers alcohol as the hydrate of an organic oxide of basic properties derives its chief support from the fact, that the oxide of ethule, when separated from its compounds, possesses the property of combining with water, and reproducing alcohol. But we cannot reproduce acetone from any of the compounds described by Kane, and which, according to him, contain the oxide of mesitule. Ether (oxide of ethule) is an oxide, because it combines with acids, atom to atom. It also forms double salts, in which one atom of acid is neutralized by the ether, another by a metallic oxide. Now, neither acetone nor oxide of mesitule form similar compounds. In the compound of Kane's oxide of mesitule with sulphuric acid, the acid retains its capacity of saturation unimpaired, and 2 atoms of sulphuric acid neutralize 2 at. metallic oxide. Consequently, the oxide of mesitule does not exist in this compound as a base, but in the same state as benzoic acid in the hyposulphobenzoic acid. Moreover, Frémy has described a substance, *Metacetone*, which has the same composition as Kane's oxide of mesitule, but very different properties. We know nothing of the real relation between those two substances and acetone.

Without, therefore, adopting Kane's theoretical views, we shall briefly describe the substances formed by him, under the names he has given them.

Mesitylene.—Formula, C_6H_4. (Kane, Plantamour.) To prepare it, acetone is distilled with half its volume of fuming sulphuric acid. On the surface of the distilled liquid swims a yellowish oil, which is washed with water and then rectified. As it sometimes contains acetone, it is again heated in the water-bath, which expels the acetone. Mesitylene, when pure, boils at 275°. When the temperature, during the rectifications, rises higher than this, it is owing to the presence of another substance, resembling mesitylene, but less volatile.

Mesitylene is an oily, colourless liquid. It has a faint and somewhat alliaceous smell.* It is lighter than water, inflammable, and burns with a white smoky flame. Alkalies do not act on it. Sulphuric acid, nitric acid, and chlorine act on it as they do on benzole. According to its formula, it contains the elements of 2 at. acetone, minus 2 water, which explains its formation.

$$2(C_3H_3O)—2HO=C_6H_4.$$

---

* By the action of sulphuric acid on the less volatile portions of the products of the distillation of caoutchouc, I obtained an oil, which in all external properties was identical with Kane's mesitylene.—W. G.

Oxide of Mesitule.—Formula, C_6H_5O. (Kane.) Obtained by acting on an alcoholic solution of chloride of mesitule by caustic potash in excess, and then adding a large quantity of water. An oily liquid separates, which is decanted, dried by contact with chloride of calcium, and rectified. It is a colourless liquid, having an odour like that of peppermint. It boils at 248°, is inflammable, and burns with a very brilliant flame and much smoke.

Chloride of Mesitule.—This compound cannot be obtained by the action of hydrochloric acid either on acetone or on the preceding substance. Its formula, according to Kane, is C_6H_5Cl; but, of several analyses, one only gave results approximating to theory. Its composition cannot therefore be considered as fully ascertained. To obtain it, 2 parts of perchloride of phosphorus are added by degrees to 1 part of acetone, the mixture being surrounded by cold water. On adding water, the chloride of mesitule separates as an oily liquid, heavier than water. Heat converts it into hydrochloric acid and mesitylene, so that it would seem that the chlorine in this compound cannot be replaced by oxygen.

Iodide of Mesitule is obtained by the distillation of a mixture of iodine, phosphorus, and acetone; but never in a state of purity. It seems to be analogous to the chloride. The residue of the distillation contains hypophospho-mesitylous acid, and another compound containing iodine, in golden-yellow scales, which Kane calls Iodide of pteleyle. (See below, p. 906.)

Chloroplatinate of Oxide of Mesitule.—Discovered by Zeise, who called it *Metacechlorplatin.*

Formula, $C_6H_5O + PtCl$.

This is a substance obtained by the action of bichloride of platinum on acetone. When distilled together, hydrochloric acid and an ethereal liquid pass over, and there remains in the retort the new substance mixed with a resinous matter, to which Zeise has given the name of *Resin of platinum.* The chloroplatinate is purified by repeated crystallizations, first in acetone acidulated with hydrochloric acid, afterwards in pure acetone. It forms small yellow crystals, not altered by a heat of 212°, but decomposed by a higher temperature, when it burns with a green flame, and leaves white metallic platinum. It is sparingly soluble in water and alcohol, insoluble in ether. When the mother-liquid of these crystals is heated, gas is disengaged, and a flocculent black powder is deposited which explodes when heated. Zeise calls it Pyracechlorplatin.

Sulphomesitylic Acid.—Formula, according to Kane, C_3H_3O, HO, SO_3. This acid has not been obtained in a separate state. When its salts are decomposed with this view, a liquid is obtained, which blackens on being evaporated, and is then found to contain free sulphuric acid, while it has the odour of sulphurous acid and oxide of mesitule.

Sulphomesitylate of Lime.—Formula, C_3H_3O, CaO, SO_3. Obtained by neutralizing with lime a mixture of 1 part of acetone and 2 parts of fuming sulphuric acid, and filtering to separate sulphate of lime. It is very soluble, deliquescent, and when heated takes fire, and leaves a residue of sulphate of lime.

Sulphomesitylate of Baryta.—Formula, C_3H_3O, BaO, SO_3. Obtained as the preceding salt. It forms pearly tables, and leaves sulphate of baryta when heated.

When 2 parts of acetone and 1 of sulphuric acid are mixed, and the mixture neutralized with lime, a new salt of lime is obtained, containing twice as much acetone for the same weight of lime and sulphuric acid.

Formula, $C_6H_6O_2, CaO, SO_3$.

Nitric Acid and Acetone.—When 1 part of fuming nitric acid is mixed with 2 of acetone, a violent reaction takes place. When the mixture has cooled, the addition of water causes the separation of a yellow oil, which consists of two different liquids. One of these is viscid, the other very fluid. The former predominates when the action has been very violent, the latter when it has been more moderate. Kane has given to the former the name of *Mesitic aldehyde;* to the latter, that of *Nitrite of oxide of pteleyle.*

Nitrite of Oxide of Pteleyle.—Formula, C_6H_3O, NO_3. It is heavier than water, and is decomposed by that liquid. Paper impregnated with it burns like tinder. It withstands a heat of 212°; but cannot be distilled without decomposition. When heated in a tube over the spirit-lamp, it explodes violently.

Mesitic Aldehyde.—Formula, $C_6H_4O_2$. Prepared as above, or by boiling mesitylene in nitric acid as long as reaction is perceived. It is a heavy, viscid, reddish-yellow liquid, of a sweetish penetrating smell. It is very soluble in alkalies, with a brown colour. It absorbs dry ammonia, and forms with it a brown resinoid mass, which is soluble in water, and may be crystallized by careful evaporation. When the liquid is rendered slightly alkaline by potash, nitrate of silver causes in it a precipitate, which, when heated in the liquid, is reduced to the metallic state. Kane considers this as a proof of the analogy of this substance to aldehyde; but the same effect is produced, in the same circumstances, by all soluble organic matters which are not acid. According to Kane, mesitic aldehyde is produced by the direct oxidation of mesitylene by the nitric acid.

Phosphomesitylic Acid.—Glacial phosphoric acid (metaphosphoric acid) is dissolved by acetone, with disengagement of heat, and production of a brown colour. When the mixture is neutralized by bases, soluble salts are obtained.

The salt of soda crystallizes in rhomboidal tables, which effloresce in the air; and, when heated, become first white, then black, and finally leave a residue of 48·8 p. c. phosphate (pyrophosphate?) of soda. (Kane.)

Hypophospho-mesitylous Acid.—The residue of the distillation of a mixture of iodine, phosphorus, and acetone, on cooling forms a mass like asbestus. Water dissolves one portion of the mass, leaving another in yellow scales undissolved. The solution has a taste both acid and bitter. When neutralized with baryta, it forms an insoluble and a soluble salt. The latter forms a crystalline mass when its solution is evaporated. This mass contains iodide of barium and hypophospho-mesitylite of baryta. Boiling alcohol dissolves the iodide of barium, and leaves the new salt, which has now become insoluble in water, and forms small crystalline grains. When heated, they burn with the flame of phosphorus, leaving a black residue, which by calcination is converted into phosphate of baryta. Nitric acid acts violently on this salt with the aid of heat. Formula of the hypophospho-mesitylite of baryta, according to Kane, $C_6H_6O_3P_2,BaO$. But he obtained by the action of nitric acid on it, 74 to 75 p. c. phosphate of baryta, indicating, not 2 at. phosphorus to 1 at. baryta, as in his formula, but 3 at. phosphorus to 2 at. baryta. Plantamour could not succeed in obtaining this salt by Kane's process.

ACTION OF CHLORINE AND IODINE ON ACETONE AND MESITYLENE.

Mesitic Chloral. — Formula, $C_6H_4Cl_2O_2$. (Dumas; Kane.) When dry chlorine gas is passed through acetone till all disengagement of hydrochloric acid has ceased, there is obtained a liquid insoluble in water, of a penetrating and offensive odour. Its sp. g. is 1·33. It boils at 260°; causes blisters on the skin; and when boiled, is decomposed with disengagement of hydrochloric acid. It is not acted on by alkalies, nor by oil of vitriol, at the ordinary temperature; but an excess of caustic potash, with the aid of heat, dissolves it, producing chloride of potassium and a new acid, the salts of which are soluble, which has not been particularly examined. The analyses made by Dumas and Kane agree in leading to the above formula; but an analysis by Liebig gave less hydrogen, with more chlorine and oxygen.

Chloride of Pteleyle.—Formula, C_6H_3Cl. (Kane.) Formed by passing chlorine through mesitylene. It separates in crystals, which are purified by solution in ether. When pure, it resembles commercial sulphate of quinine, and is insoluble in water. The analysis of this body also gave results not exactly agreeing with the formula. It is remarkable that chlorine and nitric acid act differently on mesitylene.

Iodide of Pteleyle.—This name has been given by Kane to the yellow scaly crystals obtained in the residue of the distillation of a mixture of iodine, phosphorus, and acetone. They resemble iodoforme (iodide of formule) in their properties, except that they are volatile in a high temperature without decomposition. Their composition has not been ascertained.

The formulæ which have been given for the compounds just treated of, as products of the decomposition of acetone, must be considered as the expression of a theoretical view, founded on a supposed analogy between acetone and alcohol. Before we can come to any certain conclusions in regard to these compounds, they must all be subjected to a rigid investigation.

COMPOUNDS CONTAINING ARSENIC, DERIVED FROM ACETULE.

When acetate of potash, mixed with its own weight of arsenious acid, is subjected to dry distillation, a liquid is obtained, which was discovered by Cadet, and has long been known under the name of Cadet's fuming liquor. Bunsen has lately studied this substance minutely, and has named it *Alkarsine.* It is characterized by its insupportable smell, and a high degree of spontaneous combustibility. The first analyses of this substance, by Dumas and Bunsen, left it doubtful whether its true formula was $C_4H_6As_2$, or, according to the view of Berzelius, $C_4H_6As_2O$; but the later analyses of Bunsen have decidedly established the latter formula;

and his subsequent researches have confirmed the view, first started by Berzelius, that alkarsine is the oxide of a compound radical, *Kakodule*, (from κακὸς, bad, and ὀδωδη, smell,) the formula of which is $C_4H_6As_2$, and its symbol Kd.

The following table contains the compounds of this radical already described and analysed by Bunsen, who is still occupied with the investigation of the subject, and to whose kindness the Editor is indebted for the facts now published. Only the results, however, are here stated; for the details the reader is referred to the Memoirs of Bunsen published, and to be published.

$C_4H_6As_2 = Kd$ = Kakodule (unknown).
$C_4H_6As_2,O = Kd\,O$ = Oxide of Kakodule. (Alkarsine.)
$C_4H_6As_2,S = Kd\,S$ = Sulphuret of Kakodule.
$C_4H_6As_2,Se = Kd\,Se$ = Seleniuret of Kakodule.
$C_4H_6As_2,Cy = Kd\,Cy$ = Cyanide of Kakodule.
$C_4H_6As_2,Cl = Kd\,Cl$ = Chloride of Kakodule.
$C_4H_6As_2,Br = Kd\,Br$ = Bromide of Kakodule.
$C_4H_6As_2,I = Kd\,I$ = Iodide of Kakodule.
$C_4H_6As_2,F = Kd\,F$ = Fluoride of Kakodule.
$C_4H_6As_2,Cl + HO = KdCl,HO$ = Hydrated Chloride of Kakodule.
$C_4H_6As_2,O + HgCl_2 = KdO,HgCl_2$ = Compound of Oxide of Kakodule with Bichloride of Mercury.
$C_4H_6As_2,O + HgBr_2 = KdO,HgBr_2$ = Do. with Bibromide of Mercury.
$C_4H_6As_2O + 3(C_4H_6As_2Cl) = KdO,3KdCl$ = Oxy-chloride of Kakodule.
$C_4H_6As_2O + 3(C_4H_6As_2Br) = KdO,3KdBr$ = Oxy-bromide of Kakodule.
$C_4H_6As_2O + 3(C_4H_6As_2I) = KdO,3KdI$ = Oxy-iodide of Kakodule.
$C_4H_6As_2,O_4 + HO = KdO_4,HO$ = probable formula of Kakodylic acid. (Alkargen.)

It will at once be seen, that the radical may be traced unchanged throughout all these combinations. In fact, it is exceedingly permanent, and has very strong affinities.

Oxide of Kakodule.—Syn. Alkarsine. Formula, $C_4H_6As_2,O = KdO$. (Bunsen.)

Equal weights of acetate of potash and arsenious acid are slowly heated to redness in a glass retort placed in a sand-bath and connected with a receiver surrounded with ice. Carbonic acid and some inflammable gases are disengaged, metallic arsenic sublimes; and in the receiver are found, besides the metal, two liquids, the heavier of which contains alkarsine and another heavy arseniuretted compound, while the lighter is a solution of alkarsine in water, acetone, and acetic acid. From 1 lb. of arsenious acid about 5 oz. of impure alkarsine are obtained. To purify it, the heavy liquid is agitated with water to remove acetone or acetic acid, and rectified with caustic potash in an atmosphere of carbonic acid gas. A final rectification over lime or baryta renders it anhydrous.

Alkarsine is a colourless ethereal liquid, refracting light powerfully, boiling at about 300°; at $-10°$ congealing into white silky scales. The sp. g. of its vapour by experiment was found $= 7{\cdot}555$. The calculated sp. g. is $7{\cdot}828$, according to the above formula, $C_4H_6As_2O$.

The smell of alkarsine resembles that of arseniuretted hydrogen, and is in the highest degree offensive. Its vapour irritates the eyes, causing a flow of tears. The liquid, if placed on the skin, causes violent itching. It is a powerful poison in every shape.

Oxide of kakodule is a feeble base, and combines with acids. With phosphoric and diluted nitric acids it forms viscid liquids; the latter compound produces, in metallic solutions, precipitates not yet examined. With sulphuric acid, oxide of kakodule forms white needles, of a very offensive odour, and deliquescing in the air. It is rapidly oxidized by strong nitric acid, chlorine and bromine, with the production of a new body, kakodylic acid, or alkargen. It absorbs oxygen from the atmosphere, even under water, and is converted into the same compound. When air or oxygen is freely admitted to it, it inflames spontaneously, burning with a pale flame and forming thick fumes of arsenious acid. It is sparingly soluble in water, miscible in every proportion with alcohol and ether.

The production of oxide of kakodule from acetone is very easily explained: 2 at. acetone $C_6H_6O_2 + 1$ at. arsenious acid As_2O_3 yields 1 at. oxide of kakodule, $C_4H_6As_2O + 2$ at. carbonic acid, C_2O_4.

Sulphuret of Kakodule.—Formula, $C_4H_6As_2S = KdS$. Formed by distilling chloride of kakodule with hydrosulphuret of sulphuret of barium. $KdCl + BaS,HS = KdS + BaCl + HS$. The sulphuretted hydrogen is disengaged as gas, and its presence is useful in preventing the oxidation of the sulphuret by the atmosphere. It is also formed when oxide of kakodule is acted on by the same salt, especially if an acid be present; and, finally, it is produced when sulphuretted hydrogen acts on kakodylic acid (alkargen) $KdO_4 + HO$.

$$(KdO_4+HO)+4HS=KdS+4HO+S_3.$$

Here three-fourths of the sulphur are set free.

It is a clear liquid, of a most disagreeable smell, nearly insoluble in water, and heavier than that liquid.

Seleniuret of Kakodule.—Formula, $C_4H_6As_2,Se = KdSe$. Very analogous to the sulphuret, both in smell and in other properties.

Cyanide of Kakodule.—Formula, $C_4H_6As_2,Cy = KdCy$. This compound is best formed by distilling a strong solution of bicyanide of mercury along with oxide of kakodule. Metallic mercury is deposited, part of the oxide is converted into kakodylic acid, and on applying heat the cyanide distils over. When pure it forms large brilliant crystals, easily fusible and volatile. Like all these compounds, it has a most offensive smell, and is poisonous in the highest degree. The vapour, in small quantity, causes vomiting, numbness of the extremities, fainting, and other alarming symptoms; and the utmost caution is required in experimenting on it.

Chloride of Kakodule.—Formula, $C_4H_6As_2,Cl = KdCl$. It is best prepared by distilling the compound of oxide of kakodule and bichloride of mercury mentioned in the table, with very strong hydrochloric acid.

$$KdO,HgCl_2 + HCl = KdCl + HO + HgCl_2.$$

It forms a clear liquid, very inflammable, exploding when heated in oxygen gas, and inflaming spontaneously in chlorine gas. It has a most powerful, offensive, and irritating odour, causing violent inflammation of the mucous membrane of the nose, and smarting the eyes very severely. It is also highly poisonous, and great caution is necessary in preparing it.

When exposed to the atmosphere, it deposits crystals, which Bunsen has found to be oxy-chloride of kakodule.

Iodide of Kakodule.—Formula, $C_4H_6As_2,I = KdI$.

Its preparation and properties are analogous to those of the chloride.

The *bromide* and *fluoride* of kakodule are analogous to the two preceding compounds.

The chloride, bromide, and iodide of kakodule in contact with water form each a basic compound, containing 1 at. oxide of kakodule and 3 at. of the chloride, bromide, or iodide of kakodule. The same compounds may be formed by the action of the corresponding hydracids, dissolved in water, on the oxide of kakodule.

These compounds are liquids, similar in most of their properties to the chloride, bromide, and iodide of kakodule. Their formulæ have been given in the table.

The compounds of oxide of kakodule with bichloride and bibromide of mercury are both white crystalline compounds. They are very interesting in reference to the theory of organic compounds, but we have not space here to do more than mention them. Their formulæ, according to Bunsen, will be found in the table.

Kakodylic Acid. Syn. Alkargen.—This compound is formed by the oxidation of the oxide of kakodule. Its formula is believed to be $C_4H_6As_2O_4 + HO = KdO_4 + HO$.

Air or oxygen is allowed very gradually to come in contact with alkarsine. At first cold is applied to moderate the combustion. There are formed kakodylic acid, which crystallizes; arsenious acid; and an ethereal volatile product, soluble in water, of an intolerably fetid smell, *hydrarsine*. Towards the end of the combustion the liquid forms a semi-solid mass, which is acted on by cold water. This dissolves kakodylic acid and hydrarsine, leaving the greater part of the arsenious acid undissolved. The solution is now evaporated till it forms a solid mass, which is pressed in bibulous paper to remove the hydrarsine. The pressed mass is dissolved in boiling absolute alcohol, which on cooling deposits crystals. These are again pressed in paper, and purified by repeated solution in alcohol, or repeated evaporation of the aqueous solution in the water-bath, when the last traces of hydrarsine are expelled. Arsenious acid is removed by hydrated peroxide of iron, after which the kakodylic acid is again crystallized from alcohol. Ether, added to the mother-liquid, causes the deposition of more crystals.

Kakodylic acid forms brittle, glassy, transparent, colourless, regular four-sided prisms, with unequal acuminating planes, set obliquely on the lateral surfaces. It is inodorous, nearly tasteless, permanent in dry, deliquescent in moist air, soluble in water and alcohol, insoluble in ether. It has a feebly acid reaction, and forms with the alkalies gummy, amorphous compounds. It dissolves hydrated peroxide of iron and hydrated oxide of copper with the aid of heat. It is soluble in oil of vitriol, and crystallizes from it without change. It is not decomposed by anhydrous sulphuric acid, and is with difficulty oxidized by nitric acid or aqua regia.

It melts at 390°, with partial decomposition, and congeals at about 195° to a radiated crystalline mass. At 445° it becomes brown, gives out vapours smelling of alkarsine, and deposits arsenic and arsenious acid.

When treated with protochloride of tin, phosphorous or phosphatic acid, it is converted into alkarsine by the loss of oxygen and water. In the watery solution, sulphuretted hydrogen does not cause a precipitate of sulphuret of arsenic. The liquid becomes milky, and when heated deposits oily drops of sulphuret of kakodule. Alkargene has no poisonous action on the animal body.

The remarkable compounds above described are only a part of the numerous and very interesting compounds of the new radical. But the others which have been formed are not yet so well known as to enable us to classify them properly. The chemical world looks forward with interest to the completion of Dr. Bunsen's researches into these singular substances.

It ought to be mentioned here, that we may employ these compounds in testing for arsenic. If a metallic sublimate, supposed to be arsenic, be boiled with water containing air till it is dissolved, the solution mixed with potash and acetic acid, and evaporated to dryness, the residue, when heated in a test tube, gives off the horrible smell of oxide of kakodule. If to the ignited mass a few drops of protochloride of tin be added, the still more penetrating odour of the chloride of kakodule will be perceived. Antimony does not produce these effects. This test may also be employed to recognize the acetates. (Bunsen.)

CONSTITUTION OF ETHER AND ITS COMPOUNDS.

Ether and ammonia have a certain degree of analogy in their compounds, which was first pointed out by Dumas and Boullay; and as the view taken in France of the compounds of ammonia admitted the existence of ammonia and water, as such, in the ammoniacal salts, the analogy was extended to ether, which was considered the first hydrate of olefiant gas, alcohol being the second hydrate. In Germany and other countries a different view was taken of ammonia and its compounds. The water was supposed to form an integrant part of the base; its hydrogen, with the ammonia, forming ammonium, and its oxygen uniting with the ammonium to form an oxide. This view naturally led to the idea of organic oxides of compound radicals, possessing the characters of bases, as a kind of balance to the well-known organic acids, or oxides having acid characters. Hence ether was considered as an organic oxide, of the radical C_4H_5; and the existence of these conflicting opinions gave rise to a contest of ten years' duration, the immediate result of which was the discovery of a multitude of compounds, while science was enriched with numberless important observations. No department of organic chemistry has been so thoroughly investigated as that of the ethereal compounds; and now that the existence of organic oxides is universally admitted, the contest between the two theories of ether has ceased, while it cannot be said that the question has been decisively settled by experiment. Indeed, if, in the actual state of the science, we consider the compounds of ether and ammonia, it is easy to see that the opposite opinions were essentially the same, and that men disputed about them because they were not agreed on the interpretation of the phenomena; for these two series of compounds assume the same form, if we consider amide as the radical of the ammoniacal series, and acetule as that of the series of ether. They only differ in this, that the compounds of acetule are frequently acid, which is not the case with those of amide.

Let Ad represent amide $= NH_2$, and let Ac represent acetule $= C_4H_3$. We shall then have:

COMPOUNDS OF ACETULE.	COMPOUNDS OF AMIDE.
$Ac = C_4H_3 =$ acetule.	$Ad = NH_2 =$ amide.
$AcH =$ olefiant gas.	$AdH =$ ammonia.
$AcH_2 =$ ethule.	$AdH_2 =$ ammonium.
$AcH_2O =$ ether.	$AdH_2O =$ oxide of ammonium.
$AcH_2Cl =$ chloride of ethule.	$AdH_2Cl =$ sal-ammoniac.
$AcH_2I =$ iodide of ethule.	$AdH_2I =$ iodide of ammonium.
$AcH_2Br =$ bromide of ethule.	$AdH_2Br =$ bromide of ammonium.
$AcH_2O + 1$ at. acid $=$ salts of oxide of ethule.	$AdH_2O + 1$ at. acid $=$ salts of oxide of ammonium.
$AcH_2O + HO =$ alcohol.	$AdH_2O + HO =$ compound in sulphate of ammonia.
$AcH_2S + HS =$ mercaptan.	$AdH_2S + HS =$ hydrosulphuret of ammonia (hydrosulphuret of sulphuret of ammonium).
$AcH_2O + CS_2 =$ xanthic acid.	$AdH_2S + CS_2 =$ carbosulphuret of sulphuret of ammonium.
$AcPt + PtCl_2 =$ acid in Zeise's salt.	$AdHg + HgCl_2 =$ white precipitate. (Kane.)
$AcPt,PtCl_2 + ClK =$ Zeise's salt with chloride of potassium.	$AdPtCl + AdH_2O =$ new base of Gros.
$AcPt,PtCl_2 + AdH_2Cl =$ do. with sal-ammoniac.	$AdPtCl + AdH_2Cl =$ compound of do. with hydrochloric acid.
$AcH_2 =$ olefiant gas.	
$AcH_2 + 2SO_3 =$ isethionic acid.	$AdH + SO_3 =$ Rose's anhydrous sulphate of ammonia.
$AcO =$ oxide of acetule.	
$AcCl =$ chloride of acetule.	
$AcBr =$ bromide of acetule.	
$AcO + HO =$ aldehyde.	

COMPOUNDS OF ACETULE.	COMPOUNDS OF AMIDE.
$AcCl+HCl=$oil of olefiant gas.	
$AcBr+HBr=$ corresponding compound with bromine.	
$AcCl+Pt_2Cl=$Zeise's acid.	
$Ac+CO$ . . *	$Ad+CO=$carbamide.
	$2Ad+2CO=$urea.
	$Ad+2CO=$oxamide.
$Ac+Bz=$oil of cinnamon. (Dumas.)	$Ad+Bz=$benzamide.
$AcBz+NO_5+aq.=$nitrate of oil of cinnamon.	$AdBz+C_4HO_3+aq.=$hippuric acid.
$AcH_2O+2C_2O_3=$binoxalate of oxide of ethule.	
$AcH_2,Ad+2C_2O_3=$oxamethane. (Dumas.)	
$AcO+O=$aldehydic acid.	
$AcO+O_2=$acetic acid.	
$AcO+Cl_2$ $\left.\begin{matrix}AcO+Cl\\ S\end{matrix}\right\}$ $AcO+S_2$ — compounds discovered by Malaguti, by acting on ether with chlorine, and on the new product by sulphuretted hydrogen.	

PRODUCTS OF THE SUBSTITUTION OF HYDROGEN, BY CHLORINE.	SUBSTITUTION OF HYDROGEN IN THE COMPOUNDS OF AMIDE.
$C_4H_3O+HO=$aldehyde.	$NH_2=$amide.
$C_4Cl_3O+HO=$chloral.	$NO_2=$deutoxide of nitrogen.
$C_4H_3O_3+HO=$acetic acid.	$NC_2=$cyanogen.
$C_4Cl_3O_3+HO=$chloracetic acid.	$NS_2,S=$sulphuret of nitrogen (Soubeiran).
$C_4H_3,H=$ olefiant gas.	
$C_4Cl_3,Cl=$ protochloride of carbon.	
$C_4Cl_3,Cl_3=$ perchloride of carbon, corresponding to dry acetic acid.	
$C_4Cl_3+BzCl=$chlorocinnose (Dumas).	

These formulæ require no explanation. They have been developed, in order to show the extraordinary analogy between the series of ammonia and that of ether, and to explain how olefiant gas came to be considered by many as the first member of the series of ether. They show that the two opposed theories of ether have the same foundation, and render any farther dispute about the truth of either unnecessary. It is probable that, by searching for acetule and amide in known substances, these series may be much extended

Kane first proposed to consider the compounds of ether and

---

* $Ac,CO=$oil of cloves (Dumas)? Santonine? (C_5H_3O, Ettling). $Ac,2CO=$Mannite$=C_6H_3O_2+4$ aq. Caffeine, Asparagine, and many other substances, may also be introduced into the series of acetule, although with slender probability.

ammonia, according to the above view. Malaguti also constructed a similar table, considering ether as a compound of 2 at. hydrogen with 1 at. oxide of acetule $= AcO,H_2$.

In the following pages, the different kinds of sugar, and the products of their decomposition, are considered, as an appendix to the compounds of ethule; chiefly, because from them are derived alcohol, and consequently all the compounds of ethule; and also, because the uncertainty in which we are as to their true constitution renders it impossible to arrange them on scientific principles.

SUGAR.

If we understand by sugar all those substances which are susceptible of the vinous fermentation, that is, which by a peculiar decomposition are resolved into alcohol and carbonic acid, we shall include under this head the following substances: cane sugar, grape sugar (sugar of starch, of honey, of diabetes), uncrystallizable sugar, sugar of milk or lactine, and mushroom sugar, found by Wiggers in the ergot of rye.

CANE SUGAR.

Formula, $C_{12}H_9O_9 + 2$ aq. Occurs in the juice of the sugar cane, of the maple, of beet-root, (and many similar roots, as carrots, turnips, &c.) of juglans alba, in potatoes, in the root of althæa officinalis, in the nectaries of most flowers, in the tubers of lathyrus tuberosus, &c. &c.

Pure sugar is prepared from these juices by crystallization, after they have been clarified by means of milk of lime, blood, milk, &c. When made to cool rapidly, it forms small cohering crystals, which constitute loaf-sugar, or white sugar. When slowly crystallized, it forms regular large transparent crystals, known as sugar-candy.

Sugar is colourless, but, when impure, yellow or brown; and forms hard, transparent, easily cleavable, four-sided and irregular six-sided prisms, acuminated on two surfaces, sp. g. 1·6065, friable, phosphorescent when rubbed in the dark, permanent in dry air. At 365°, (285°, Proust,) according to Peligot, it melts into a viscid colourless liquid, which by sudden cooling forms an amorphous transparent mass (barley-sugar). This, when kept, becomes opaque and brittle, and then shows the usual planes of cleavage of sugar. At 400° to 420° sugar is converted into caramel, losing 3 at. water. At a higher temperature it yields combustible gases mixed with carbonic acid, empyreumatic oil, acetic acid, and a residue of one-fourth of its weight of carbon. (Cruikshank.)

Cane sugar dissolves in one-third of its weight of cold water, in hot water to any extent. A solution, saturated at 230°, forms on cooling, a mass composed of small cohering crystals. A solution saturated in the cold has a viscid consistence, and is called syrup. If kept long at a temperature near the boiling point, the syrup loses the power of crystallizing. When syrup is boiled, the bubbles of vapour burst with an audible noise, owing to the viscidity of the liquid. One-twentieth part of oxalic, citric, or malic acids, instantly renders the boiling syrup thin, and deprives the sugar of the power of crystallization, which cannot now be restored by means of alkalies, although the sugar is still capable of undergoing fermentation. When heated with dilute sulphuric acid (Kirchhof, Pelouze), or with tartaric acid (Guibourt), it is converted into grape sugar.

Oil of vitriol dissolves sugar with a brown colour. If the superfluous acid be removed by chalk, there remains a compound of sugar with sulphuric acid, which blackens on evaporation, with disengagement of sulphurous acid (Braconnot). This compound is *saccharo-sulphuric acid*, which is accompanied by a brown substance, also possessed of acid properties. When loaf-sugar is moistened with oil of vitriol, a violent reaction takes place after some time, sulphurous and formic acids being disengaged. The sugar forms a soft coal-black paste, which, when washed with water, leaves a black carbonaceous powder. Sugar, when kept for a long time at a high temperature dissolved in dilute sulphuric acid, absorbs oxygen from the air, formic acid is produced, and a brown insoluble matter is deposited, which Malaguti considers identical with the matter formed by the decay of wood to which the name of *humus* or *humic acid* has been given.

Hydrochloric acid readily dissolves sugar, and forms a black, thick, resinous paste. Nitric acid changes it into saccharic, oxalic, and carbonic acids: 100 parts of sugar yield 54 (Cruikshank), or upwards of 67 (Thenaud), of oxalic acid.

When arsenic acid is added to syrup, the mixture after some hours becomes pink, then purple, and lastly brown, and the odour of acetic acid is perceived. Acids and alkalies do not change this colour. If all the arsenic be precipitated by sulphuretted hydrogen, there remains a pale yellow sweet liquid, not precipitated by acetate of lead. (Elsner.)

Cane sugar dissolves carbonate of copper and verdigris, forming green solutions, from which the oxide is not precipitated by alkalies. The salts of oxide of copper and peroxide of iron, when mixed with sugar, are no longer precipitable by alkalies. Hydrated oxide of copper dissolves with the aid of alkalies in a solution of sugar, with a violet colour. When all these solutions are heated, metallic copper or suboxide of copper is precipitated, the latter sometimes pure, and sometimes mixed with a brown substance soluble in ammonia; and the liquid contains formic acid. (Wöhler.) A solution of cane sugar, heated with nitrate of silver, causes a black precipitate.

Bichloride of mercury is reduced to calomel, and chloride of copper to subchloride, by the action of sugar; and chloride of gold in the same circumstances yields a red precipitate.

Chlorine gas, passed through a boiling solution of sugar, decomposes it. Hydrochloric acid is formed, along with another uncrystallizable acid (Simonin), malic acid? (Chenevix). According to Liebig, this decomposition is very incomplete. Sugar in powder slowly absorbs moist chlorine, and is changed into a brown deliquescent mass, containing hydrochloric acid, while carbonic acid is disengaged (Priestley, Bouillon Lagrange, Vogel). Dry chlorine passed over dry sugar does not act on it. (Liebig.)

Sugar is much employed, from its antiseptic power, to preserve vegetable and animal matters. In pharmacy it is used for syrups, electuaries, conserves, &c. Sugar, taken along with other food, is a nourishing article of diet; but if taken alone, or at least without any nitrogenised substance, it cannot long support life. (Magendie.)

Biot has observed, that a ray of polarized light, when passed through a solution of cane sugar, exhibits in the plane of polarization a succession of the prismatic colours, when that plane is turned round to the right hand.

Cane sugar forms with the alkalies, with oxide of lead, and with common salt, what appear to be saline combinations.

It is sparingly soluble in cold alcohol, and requires 80 parts of boiling alcohol for solution; but 4 parts of spirit of wine, sp. g. 0·880, dissolve 1 of sugar.

COMBINATION OF SUGAR WITH BASES.

The property possessed by sugar, of combining with certain bases,—of dissolving, for example, a much larger quantity of lime than pure water,—has long been known. Berzelius and Peligot have analyzed the compound of sugar with oxide of lead, and Peligot those with baryta and lime.

In these compounds crystallized sugar loses 1 eq. water, which is replaced by 1 eq. of metallic oxide or chloride of sodium. The following are the formulæ of these compounds:

$C_{12}H_9O_9 + 2HO$ =crystallized cane sugar.

$C_{12}H_9O_9 + \left.\begin{matrix}HO\\BaO\end{matrix}\right\}$ =compound with baryta.

$C_{12}H_9O_9 + \left.\begin{matrix}HO\\CaO\end{matrix}\right\}$ =compound with lime.

$C_{12}H_9O_9 + 2PbO$ =compound with oxide of lead.

$2(C_{12}H_9O_9) + \left.\begin{matrix}3HO\\NaCl\end{matrix}\right\}$ =compound with common salt.

The two first compounds dissolve several metallic oxides, when an excess of sugar is added. Probably double compounds are formed, but these have not been obtained in crystals. The solutions of these two compounds have a strong alkaline reaction, and absorb carbonic acid readily from the air, while a certain quantity of sugar is set free, giving a sweet taste to the compound. In the dry state they may be preserved without change. When kept dissolved, an excess of alkali appears to facilitate their decomposition. Braconnot observed, that a solution of the compound with lime, kept for four years in a bottle imperfectly stopped, deposited a precipitate composed of carbonate, oxalate, and another salt of lime, the acid of which was uncrystallizable, very sour, and gave with salts of lead, or with lime-water, a precipitate soluble in an excess of the acid. The liquid still contained uncrystallizable sugar, and a peculiar substance combined with lime, which was precipitated by alcohol as a viscid mass. Sulphuric acid, added to the same liquid, formed a precipitate of sulphate of lime, disengaging acetic acid.

A solution of cane sugar, boiled with excess of caustic potash, is gradually changed into grape sugar, which itself is converted by the alkali into potassio-saccharic acid. (Peligot.)

Powdered sugar absorbs ammoniacal gas, and is changed into a flexible mass, compact and crystalline at the surface, and smelling strongly of ammonia. (Berzelius.)

Indigo in contact with solution of sugar and potash, or soda in excess, easily yields oxygen to the sugar, and is converted into deoxidized or white indigo. The sugar is changed into formic acid. (Wöhler.)

Compound of Sugar with Lime.—Formula, $C_{12}H_9O_9 + \begin{matrix} CaO \\ HO. \end{matrix}$ (Peligot.) By exposing to a moderate heat a solution of sugar along with hydrate of lime, there is obtained a bitter alkaline liquid, containing, for 100 parts of sugar, according to Daniell, 50 parts; according to Osann, 56 parts of lime. This solution, when boiled, becomes turbid, and forms a gelatinous mass, like the jelly of starch, but becomes again liquid by cooling. (Löwitz; Osann.) The precipitate is a compound of sugar and lime, atom to atom, containing 14 p. c. of lime. It is purified by washing with boiling water, in which it is insoluble; or it may be obtained by adding alcohol to the solution of lime with excess of sugar.

The solution of this compound exposed to the air deposits regular acute rhomboids of hydrated carbonate of lime. (Pelouze.)

Compound of Sugar with Baryta.—Formula, $C_{12}H_9O_9 + \begin{matrix} HO \\ BaO. \end{matrix}$ By mixing a solution of 1 part of baryta in 3 of water with a solution of 2 parts of sugar in 4 of water, there is obtained, after some time, a crystalline semi-solid mass, which is increased by a gentle heat. It is washed with cold water, care being taken to avoid the contact of carbonic acid; the dry compound forms small brilliant crystals in foliated scales like boracic acid.

The solution of these crystals has an alkaline taste and reaction. Carbonic acid and other acids restore the sweet taste by neutralizing the base, and setting free the sugar.

Peligot, who analyzed this compound, found 28·1 p. c. of carbon, 4·14 of hydrogen, and 31 of baryta; and, not having reckoned that portion of the carbon ($\frac{1}{12}$th) retained by the baryta, he adopted the formula, $C_{12}H_9O_9 + \left.\begin{matrix} 2HO \\ BaO \end{matrix}\right\}$. When this correction is made, however, his analysis corresponds exactly to the formula, $C_{12}H_9O_9 + \left.\begin{matrix} HO \\ BaO \end{matrix}\right\}$, which is also much more probable. According to the first, sugar combines with baryta without losing water; according to the latter, one equivalent of water is replaced by one equivalent of baryta.

Compound of Sugar with Oxide of Lead.—Formula, $C_{12}H_9O_9 + 2PbO$. (Peligot.) A boiling solution of sugar dissolves oxide of lead, and deposits a white precipitate, which is obtained quite pure by washing with boiling water. The mother-liquid contains a soluble compound of sugar with oxide of lead.

A mixture of a concentrated solution of sugar with one of acetate of lead deposits a gelatinous precipitate, which is to be washed with cold water, and afterwards dissolved in boiling water. This solution, left to itself in a closed bottle, deposits the salt gradually in the form of white mammillary groups of crystals. These are washed with cold water, and dried in vacuo, or in a box beside quicklime. Berzelius, who also analyzed this compound, obtained 58·26 p. c. of oxide of lead, and adopted the formula, $C_{12}H_{10}O_{10} + 2PbO$. But Peligot, on repeating his analysis, succeeded in proving satisfactorily that the salt contains 59 p. c. oxide of lead, and the other elements in proportions exactly corresponding to the formula, $C_{12}H_9O_9 + 2PbO$.

Compound of Sugar with Chloride of Sodium.—Formula, $2(C_{12}H_9O_9) + \left.\begin{matrix}3HO\\ NaCl\end{matrix}\right\}$. (Peligot.) This compound is obtained by the spontaneous evaporation of a solution of 1 part of common salt, and 4 parts of sugar. Candy sugar is first deposited, and the solution, decanted off these crystals, at last deposits the new compound. It has a taste both sweet and saline, and deliquesces in a moist air.

GRAPE SUGAR.

Syn. Glucose (Dumas); Diabetic Sugar; Sugar of Starch; Sugar of Fruits. Formula, $C_{12}H_{14}O_{14}$. The sweet taste of grapes, of most acid fruits, of honey, &c. proceeds from this kind of sugar. It is also a product of the decomposition or transformation of a variety of substances. Thus, cane sugar, starch (Löwitz), woody fibre (Braconnot), sugar of milk (Vogel), when treated with dilute acids, furnish grape sugar. Starch yields it, according to De Saussure, by spontaneous decomposition; according to Kirchhof, by the action of the gluten of malt. It is found ready formed in the urine of persons affected with diabetes mellitus.

To obtain the sugar contained in ripe grapes, the juice is neutralized with chalk, clarified by white of egg, and evaporated till it crystallizes. From dry raisins it is obtained by pounding them, and acting on the mass with cold alcohol to remove the uncrystallizable sugar, pressing the whole, redissolving in water, neutralizing with chalk, clarifying as before, and evaporating. Fresh honey appears to contain grape sugar in a particular state. In the comb it forms a clear syrup, very viscid, and retains this character if kept in a dry place; but when separated from the wax, by melting in water, a diluted liquor is obtained, which after some days forms a crystalline mass, having more consistence than the honey, although containing one-fourth of its volume of water in addition. The solid parts of this mass are grape sugar.

It may be extracted from diabetic urine by evaporating that liquid till it crystallizes. The crystals are washed on a filter with cold alcohol, and the white residue is redissolved in water and purified by recrystallization.

To convert sugar of milk into grape sugar, 100 parts are dissolved in 400 of water, 2 parts of sulphuric acid are added to the mixture, and the whole is exposed to a temperature near the boiling point for three or four hours. The liquid is then neutralized with lime or baryta, to separate the sulphuric acid, and evaporated to a syrup, when the grape sugar crystallizes after three or four days.

Preparation of Grape Sugar from Starch.—1. By sulphuric acid. One part of potato starch, 4 parts of water, and from $\frac{1}{100}$th to $\frac{1}{10}$th of sulphuric acid are boiled for thirty-six to forty hours, renewing from time to time the water as it evaporates. Under a high pressure, or at a higher temperature, the change may be effected in a shorter time and with a smaller proportion of sulphuric acid. When a thin paste of starch and water is slowly poured into the boiling diluted acid, it speedily loses the consistence of jelly which it at first acquires; and, when the operation is performed on the large scale, the contact alone with the dilute acid for ten or twelve hours is sufficient to change the starch into grape sugar, provided the mixture is not allowed to cool too rapidly.—2. By means of malt. The paste of starch speedily loses its gelatinous consistence if an infusion of malt be poured on it. It then forms a mobile liquid, and if there be enough of malt, the starch is completely changed into grape sugar at the end of some hours, provided the mixture be kept at the temperature of 160° to 170°. Six parts of malt produce on an average 25 parts of grape sugar. As soon as the liquid ceases to strike a blue colour with iodine, or to be precipitated by acetate of lead or alcohol, we may be certain that all the starch is changed into grape sugar.

Preparation of Grape Sugar from Woody Fibre.—Twelve parts of linen or paper cut in small pieces are intimately mixed by degrees with 17 parts of strong sulphuric acid (Braconnot); or what is better, with 5 parts of sulphuric acid and 1 of water (Vogel). All rise of temperature must be carefully avoided. After twenty-four hours, the pitchy mass is dissolved in a large quantity of water, and boiled for ten hours. The liquid is then neutralized with chalk, filtered, and, after evaporating to the consistence of syrup, the residue is set aside to crystallize.

According to Brunner, 100 parts of starch produce 104 to 106 of grape sugar. According to De Saussure, 110, and according to Braconnot, 100 parts of linen rags yield 114 of sugar, and even 115·7, according to Guérin. By calculation 100 parts of starch, by combining with 4 atoms of water for 1 of starch, should yield 122·03 parts of crystallized grape sugar.

If we compare the composition of starch, sugar of milk, woody fibre, and cane sugar with that of grape sugar, we perceive that they all contain the same quantity of carbon, united with different quantities of oxygen and hydrogen in the proportions to form water; and that grape sugar contains the most oxygen and hydrogen. We obtain exactly the composition of crystallized grape sugar by adding 6 atoms of water to the elements of 1 atom lignine (woody fibre), 4 atoms to starch, 3 atoms to cane sugar, and 2 atoms to crystallized sugar of milk.

In what manner does malt act in converting starch into sugar? This question is yet to be answered. As to the action of sulphuric acid on starch, it appears to be quite analogous to the formation of ether by the decomposition of bisulphate of oxide of ethule. At least, starch and sulphuric acid form a crystalline compound, according to De Saussure, and a gummy compound described by Guérin; these compounds are neutral, and are resolved by boiling into grape sugar and free sulphuric acid.

Before becoming grape sugar, starch is converted into a substance resembling gum, which gives a wine-red colour with iodine. Payen and Persoz have called it *Dextrine*, because it has the property of causing the rays of polarized light to deviate to the right hand. Frémy has observed that in the conversion of starch into grape sugar, there is obtained a variable quantity of *mannite*.

It appears that the quantity of grape sugar in diabetic urine has a direct proportion to the quantity of fecula in the food of the patient, such as bread, potatoes, &c. But as the experiments of

Gerhardt have shown that animal gelatine, acted on by sulphuric acid, yields fermentescible sugar, we may naturally suspect that the proximate principles of the body are also concerned in the production of sugar in diabetes.

Grape sugar crystallizes from an alcoholic solution in square tables or hard transparent cubes. (De Saussure.) A concentrated aqueous solution forms on standing a spongy mass, composed of minute crystalline grains. It often happens, in crystallizing grape sugar on a large scale from a moderately strong syrup, that there are deposited hard hemispherical masses composed of needles radiating from a centre. The sp. g. of grape sugar is 1·386. (Guérin.)

Grape sugar is less soluble, and dissolves more slowly in water than cane sugar; it is much sweeter when dissolved than in the solid form: 2½ parts of grape sugar are required to produce in a liquid the same intensity of sweetness as is caused by 1 part of cane sugar.

At 212° grape sugar melts, losing 9 p. c. = 2 at. water. When heated beyond 285°, it passes into caramel. The sugar produced from starch by malt becomes soft at 140°, pasty at 158°, and syrupy between 194° and 212°, losing 9·8 p. c. of water. (Guérin.) It is soluble in 1½ parts of cold water, and to any extent in boiling water. The syrup which it forms is less viscid than that of cane sugar.

It is very soluble in cold alcohol; at 77° it dissolves in 8 parts of alcohol of 85 p. c. and in 20 parts of absolute alcohol. Almost the whole of the sugar dissolved by boiling alcohol is deposited, on cooling, in crystalline grains, which contain alcohol in combination.

It has been already mentioned that a ray of polarized light, passed through a solution of cane sugar, produces in the plane of polarization a suite of coloured rings when the plane of polarization is made to rotate from left to right. Uncrystallizable cane sugar, and the sugar in the juice of the grape, produce the same phenomenon by a rotation from right to left; as do also, although with less brilliancy of colours, crystallized grape sugar, sugar of starch, and diabetic sugar. This characteristic property is in no way affected by the commencement of fermentation in these latter kinds of sugar, but the case is different with cane sugar. As soon as it is made to ferment, the coloured rings are no longer visible by rotation from left to right, but appear as soon as the plane of polarization is made to rotate from right to left. (Biot.)

The reactions of grape sugar with acids and alkalies essentially distinguish it from cane sugar. Thus, oil of vitriol chars cane sugar, and diluted sulphuric acid converts it into an insoluble brown matter; while oil of vitriol dissolves grape sugar, producing only a slight yellow or brown colour, and forms with it a new acid, not precipitable by baryta—(sulpho-saccharic acid). On the other hand, alkalies, which do not alter the colour of cane sugar, even by boiling, provided the solutions be dilute, convert grape sugar into a brown or black substance with the aid of heat.

Peroxide of lead forms with grape sugar, at 212°, bibasic formiate of lead, water, and carbonate of lead. (A. Sturenburg.)

The compounds of grape sugar with lime, baryta, and oxide of lead, are prepared with difficulty; while it forms with ease a crystallized compound with common salt.

Although the identity of the different kinds of sugar classed under the name of grape sugar or *glucose* be generally admitted, it is important to know that there are certain facts apparently irreconcileable with this notion. For example, diabetic sugar, dried in vacuo, is represented, according to Peligot and Prout, by $C_{12}H_{14}O_{14}$; while sugar of starch prepared by malt, according to Guérin, loses in vacuo 2 at. water, and becomes $C_{12}H_{12}O_{12}$.

All experimenters on this subject agree that the sugar made from starch by sulphuric acid, the sugar of honey, and that made with malt, melt before 212°, and lose water. All these facts would go to show that the formula $C_{12}H_{14}O_{14}$ does not correspond to its composition at this temperature; but De Saussure, on the other hand, obtained in the analysis of grape sugar, crystallized, and dried at 212°, results closely agreeing with that formula.

GRAPE SUGAR WITH BASES.

Peligot and some other chemists consider cane sugar and grape sugar as bodies which act towards bases like acids, producing with them regular salts, which they call Saccharates. To this view Graham objects, that no acid is known which does not combine with potash and soda; which none of the sugars do. He considers sugar as a hydrated body, analogous rather to a hydrated salt, in which a certain portion of water is contained in a form different from water of crystallization, and may be replaced by oxide of lead, lime, or baryta, producing basic salts. Potash, soda, and oxide of silver, on the contrary, never replace but the truly basic water in a compound; for which reason these bases form no subsalts (basic salts). This explains why they do not combine with sugar. Although these views of Graham are not absolutely established, since bodies exist, such as allantoine and others, capable of uniting with oxide of silver, although we cannot make them unite with potash, soda, or baryta, yet when we reflect that sugar easily combines with common salt, forming a compound exactly like a double salt, we must admit that they acquire a high degree of probability.

If the compounds of sugar with bases are to be considered as salts, and sugar as an acid, we must also consider pyroxilic spirit as an acid; for it combines with lime and baryta, exactly like sugar, and also unites with chloride of calcium.

Grape Sugar and Common Salt.—This compound crystallizes in fine double six-sided pyramids; and is the only compound of grape sugar the composition of which is known with certainty.

It is obtained by saturating with sea-salt a moderately strong solution of grape sugar, and evaporating gently. Chloride of sodium is first deposited, and afterwards the bottom of the vessel is covered with crystals of the compound, easily recognized by their form and their hardness. They are purified by repeated crystallizations. They are colourless, transparent, friable, soluble in water, very sparingly soluble in alcohol of 96 p. c.

According to the recent analyses of Erdmann and Lehmann, these crystals contain water, and lose 2 at. = 4·337 p. c. at 212°. According to Peligot, they lose at 320°, 3 at. water = 6·1 p. c. The crystals are $2(C_{12}H_{12}O_{12}) + NaCl + 2HO$.

The compound dried at 212°, according to Erdmann and Lehmann, is $2(C_{12}H_{12}O_{12}) + NaCl$. According to Peligot, when dried at 320°, the compound is $C_{24}H_{23}O_{23} + NaCl$. But Erdmann states that, after exposure to that temperature, it no longer contains sugar, but a modified matter. This, at all events, is the case when the compound is formed from diabetic sugar, sugar of starch, or sugar of dried raisins.

Grape Sugar and Oxide of Lead.—To prepare it, a solution of acetate of lead, to which ammonia has been added, is mixed with an excess of solution of sugar. The precipitate ought to be washed and dried in vacuo at the ordinary temperature. When dried in vacuo at 300°, it becomes yellow. With the aid of heat a solution of grape sugar dissolves a large quantity of oxide of lead; but the insoluble basic compound is difficult of preparation in this way, as the mixture cannot be boiled without becoming brown. One hundred parts of crystallized grape sugar, in combining with oxide of lead, lose 11·14 p. c. of water; the residue is brown, and has the smell of caramel, even when the temperature has not exceeded 140°. (Berzelius.) This loss corresponds to 5 at. water for 2 at. crystallized sugar. Hence, the substance combined with oxide of lead must be $C_{24}H_{23}O_{23}$; which is the same as that found by Peligot in the compound with common salt, when dried at 320°.

The insoluble compound obtained from grape sugar and the ammoniacal acetate of lead has been analyzed by Peligot, who states its formula to be $C_{24}H_{21}O_{21} + 6PbO$. This would imply that the crystallized sugar lost 7 at. water, which were replaced by 6 at. oxide of lead. But on recalculating Peligot's analysis, his results will be found to agree more closely with the formula $C_{12}H_{11}O_{11} + 3PbO$, according to which 3 at. water are replaced by 3 at. oxide of lead. As this is in accordance with all our experience of such substitutions, we must reject Peligot's formula. It will then appear that the grape sugar in this compound with oxide of lead has the composition of crystallized cane sugar.

Grape Sugar with Lime and Baryta.—These bases are freely dissolved by solution of grape sugar, diminishing its sweetness. The solutions are alkaline, and become brown when heated. When lime enough is added to destroy the sweet taste, there is obtained by cautious evaporation a viscid mass soluble in alcohol. An excess of lime produces a basic compound, which alcohol precipitates in a coagulum. This precipitate, washed with alcohol, forms a white mass, which becomes semi-transparent by attracting moisture from the air. When dried, and it is difficult to dry it without turning it brown, it contains 24·26 p. c. of lime; which indicates that 2 at. lime have replaced 2 at. water in the sugar. When decomposed by carbonic acid, it yields unaltered sugar.

Peligot obtains a compound of grape sugar with baryta, by dissolving them separately in pyroxylic spirit, and mixing the solutions, that of the sugar being in excess. A flocculent precipitate is formed, which, when washed with pyroxylic spirit, pressed in bibulous paper, and dried in vacuo beside oil of vitriol and quicklime, appears as a light porous powder. The presence of water causes it to turn brown in drying. When dried at 212°, it becomes yellow, and contains 35·37 p. c. of baryta; and its formula, according to Peligot, is $(2C_{12}H_{14}O_{14}) + 3BaO$. But this is very improbable, as it would imply that 2 atoms of crystallized sugar combine with 3 atoms of baryta, without losing water, even at 212°; whereas the sugar alone loses 2 atoms of water at 212°. It appears, moreover, that Peligot omitted to reckon the amount of carbonic acid which must have remained in the combustion tube in combination with the baryta.

SULPHO-SACCHARIC ACID.

Discovered by Peligot.—To prepare it, 1 part of sugar of starch is melted in the water-bath, and mixed with 1½ parts of oil of vitriol, taking care to add the acid gradually, to agitate well, and to keep the mixture cold, if necessary, by plunging the vessel into cold water. If this be neglected, or if the sugar be impure, the product is coloured. The whole is dissolved in water, and saturated with carbonate of baryta, which precipitates the free sulphuric acid, while the sulpho-saccharate of baryta remains in solution. When this solution is treated with subacetate of lead, the precipitate first formed is coloured, and is separated; that which falls afterwards is white. Peligot analyzed it after drying it at 212°. Of two analyses, one led to the formula $2(C_{12}H_{10}O_{10}),SO_3 + 4PbO$; the other to the formula $2(C_{12}H_{12}O_{12}),SO_3 + 4PbO$. As the object of the author was merely to prove the existence of the acid, we are at present ignorant of its true composition. From the salt just mentioned, the acid may be obtained by means of sulphuretted hydrogen.

The sulpho-saccharic acid forms a sweet liquid, slightly acid, reddening vegetable blues, but not precipitating the salts of baryta, and forming soluble salts with almost all bases. It is decomposed by evaporation at a gentle heat, or even at the ordinary temperature in vacuo, being resolved into sugar and sulphuric acid, which now precipitate the salts of baryta.

PRODUCTS OF THE DECOMPOSITION OF CANE SUGAR AND GRAPE SUGAR.

By the prolonged action of a high temperature and a small quantity of diluted sulphuric acid, cane sugar passes into the state of grape sugar which has the property of combining with sulphuric acid. There is every reason to believe that the modification which small quantities of organic acids produce in cane sugar at the boiling temperature is of the same nature; that is, that grape sugar is produced, which instantly unites with the acid that has been added.

These new combinations have a sweet taste, and may be made to enter into fermentation by means of a small quantity of ferment; but they are uncrystallizable, and, when much concentrated by heat, solidify into an amorphous mass, which absorbs moisture from the air, and is again converted into syrup. Tartaric, oxalic, citric, malic, kinic, and even acetic acids, form such compounds, and thus impede the crystallization of sugar; alkalies can no longer remove the acid, nor restore to the sugar the power of crystallizing. This is the reason why we cannot obtain crystallizable sugar by evaporating the sweet juices of plants which have an acid reaction. The syrup which they yield has every property of sugar, except that of crystallizing. It was formerly considered a separate species of sugar, and described as sugar of molasses; but it is now known with certainty to be common sugar, combined with acids.

The molasses, or treacle formed in the refining of cane sugar, contains the products of the decomposition of sugar by alkalies.

ACTION OF ACIDS ON SUGAR.

A cold solution of cane sugar, with a little dilute sulphuric acid, is by degrees entirely converted into grape sugar; while the same acid, if concentrated, rapidly chars it. Now we have seen that grape sugar may be triturated with strong sulphuric acid without blackening; it is therefore obvious that the change produced by the acid when it chars cane sugar must take place before it has been converted into grape sugar.

Strong hydrochloric acid acts like sulphuric acid; when diluted and boiled with the sugar, it converts it into a solid, brown, gelatinous mass, soluble in water with a brown colour, which is purified by repeated washing with water.

The aspect and external properties of this substance do not vary, whatever be the strength of the acid or the heat employed; but its composition is totally changed. Thus when sugar is boiled with 1 part of hydrochloric acid, diluted with 1 part of water, the product when dry is a brown or brownish black powder, extremely light; its formula, when dried at 284°, is $C_{24}H_{11}O_9$. (Stein.) Along with this substance are produced formic acid and grape sugar. With a weaker acid, and at a lower temperature, there are formed two reddish-brown substances; one soluble in alkalies, the other insoluble. The formula of the insoluble compound is $C_{40}H_{16}O_{14}$; that of the other is $C_{40}H_{14}O_{12}$. By the influence of a prolonged boiling with a stronger acid, there are formed two black substances: one soluble in alkalies, the formula of which is $C_{40}H_{12}O_{12}$; the other insoluble, the formula of which is $C_{40}H_{16}O_{12}$. (Mulder.)

By boiling sugar with dilute sulphuric acid, Malaguti and Boullay obtained two substances which they considered identical with ulmine and ulmic acid, and to which therefore they gave these names; but there is every reason to believe that these substances only resemble the products of the decomposition of woody fibre in their colour, and that their chemical properties are different. One of these bodies is soluble in ammonia and the fixed alkalies, the other insoluble. We shall call the former *sacchulmic acid*, and the latter *sacchulmine.*

Sacchulmine is obtained by boiling for a very long time cane sugar in very diluted sulphuric, hydrochloric, or nitric acids. For 10 parts of sugar, 30 of water and 1 of sulphuric acid may be taken. The sacchulmine is deposited in brown scales, crystalline and brilliant, which are always contaminated with sacchulmic acid. The latter is easily removed by ammonia, in which it is soluble.

Sacchulmic Acid.—Formula, $C_{30}H_{15}O_{15}$. (Malaguti.) This acid dissolves in ammonia and the fixed alkalies, giving them a brown colour. It is precipitated from the solutions by acids as a brown flocculent powder. The alkaline earths and metallic salts also cause brown precipitates in these solutions.

When dry, it is a light brown powder, insoluble in alcohol and ether. By long boiling in water it is converted into sacchulmine, thus losing its solubility in alkalies, without any change of composition.

According to Malaguti and Boullay, the analysis of this acid leads to the formula C_2HO; but the salt which it forms with oxide of copper contains from 10 to 11 p. c. oxide of copper, which leads to the atomic weight of 4061 for the acid, and consequently to the formula $C_{30}H_{15}O_{15}$, a multiple of the above. It would appear to combine with oxides without losing water; but it is still uncertain whether the acid in the salts has the same composition as the free acid.

When sugar is boiled with dilute sulphuric acid for several days in open vessels, there is produced, besides these substances, formic acid, by means of the oxygen of the atmosphere. From 20 parts of cane sugar, 60 of water, and 1 of sulphuric acid, boiled for eighty-four hours, Malaguti obtained 6·5 parts of sacchulmine and sacchulmic acid, and 2·236 parts of dry formic acid. The formic acid is not produced when air is excluded.

PRODUCTS OF THE ACTION OF ALKALIES ON SUGAR.

Cane sugar is not coloured by being boiled with aqua potassæ, or with lime or barytic water; but if the heat be prolonged, and air admitted, the liquid becomes brown, and formic acid is produced, which combines with the alkali. The liquid contains, besides, two new acids, of which one is brown, and insoluble in water; the other is colourless, and attracts water from the air. Dumas has called these acids, which were discovered by Peligot, *Melassic Acid* and *Glucic Acid.* In this operation the cane sugar is probably first converted into grape sugar, which is rapidly changed by alkalies into these acids.

Glucic Acid.—To prepare this acid, a solution of grape sugar is saturated with baryta or lime, and left to itself. After some weeks the liquid has no longer an alkaline reaction, and the base it contains can no longer be precipitated by a current of carbonic acid. By adding subacetate of lead, a bulky white precipitate is formed, which, when decomposed by sulphuretted hydrogen, yields an aqueous solution of the acid.

This acid is very soluble in water; when dried in vacuo, it forms an uncrystallized mass like tannin. It attracts rapidly the moisture of the air. Its solution has a decidedly sour taste, and reddens litmus. All its neutral salts are soluble. The basic salt of lead alone is insoluble. Peligot, who analyzed this salt, gives for it the formula $C_{24}H_{15}O_{15} + 6PbO$. But as the analyses have not yet been sufficiently multiplied to fix its composition, we may observe that the formula $C_{12}H_8O_8 + 3PbO$ corresponds still better to the results of his analysis. Either formula will explain the formation of the acid; for as grape sugar, in the compound it forms with lead, has the formula $C_{12}H_{11}O_{11}$, to form glucic acid it has lost 3 at. water, which are replaced by 3 at. oxide of lead. Or if we consider anhydrous glucic acid to be $C_{24}H_{15}O_{15}$, and anhydrous grape sugar to be $C_{24}H_{21}O_{21}$, they will differ by 6 at. water.

Melassic Acid.—This acid is produced by the combined action of alkalies and heat on grape sugar. When a hot saturated solution of baryta or a solution of caustic potash or soda is mixed with melted grape sugar, the latter is dissolved with heat and disengagement of the vapour of water. The mixture acquires a brown colour, which becomes more and more intense if the heat be continued. Glucic acid is first formed, by the decomposition of which melassic acid is produced. The dark-brown solution is treated with excess of hydrochloric acid, which precipitates the melassic acid as a black flocculent powder. It is washed, first with diluted muriatic acid, afterwards with water.

Peligot analyzed it, and from his results Dumas has deduced the formula $C_{24}H_{12}O_{10}$.

Besides melassic acid, there is found in combination with the alkali a substance which is not volatile, and which reduces the salts of silver with great facility. Qu. Is not this saccharic acid?

ACTION OF HEAT ON SUGAR.

Caramel.—Cane sugar melts at 365° into a viscid colourless liquid, which on cooling forms a transparent amorphous mass (barley-sugar). At a temperature somewhat higher, it becomes brown; at from 400° to 430° it swells up, and is converted into a black porous mass, having a high lustre, like anthracite, called by Peligot *Caramel.* In this operation water alone is expelled, with a minute trace of empyreumatic oil and acetic acid.

The caramel of commerce contains a variable proportion of sugar. It is purified from sugar, and from certain bitter compounds which are always present in burnt sugar, by dissolving it in water and adding alcohol, which precipitates the caramel in a state of purity, retaining in solution the foreign matters.

Pure caramel is a black or brownish black powder. It dissolves readily in water, giving it a fine sepia tint. Its solution has no taste, and no action on vegetable colours. It is not susceptible of fermentation, and is insoluble in alcohol.

The solution of caramel precipitates the salts of baryta and the basic salts of lead. The composition of the barytic precipitate is variable; it contains from 20 to 21 p. c. of baryta.

When sugar is still more strongly heated, the caramel loses an additional quantity of water, and forms an insoluble compound. At a still higher temperature inflammable gases are given off, and a bulky coal is left, difficult of combustion.

According to Peligot, caramel has the same composition as cane sugar in its compound with oxide of lead, that is, $C_{12}H_9O_9$. Crystallized cane sugar, therefore, to form caramel, loses 2 at. of water. Grape sugar produces the same substance when similarly treated.

Metacetone.—Formula, C_6H_5O. (Fremy.) This substance is obtained by distilling an intimate mixture of 1 part of sugar and 8 parts of finely powdered quicklime. When the temperature reaches 285°, it suddenly rises of itself, and there is disengaged a small quantity of an inflammable gas, with an inflammable liquid, which is a mixture of acetone and metacetone. The addition of water separates the metacetone, which is purified by rectification, the last portions which distil being preserved.

It is a colourless liquid, having a pleasant odour. It boils about 183°, is miscible with alcohol and ether, but not with water. It may be regarded as acetone minus 1 at. water.

$$C_6H_6O_2-HO=C_6H_5O.$$

One atom of anhydrous sugar contains the elements of

½ at. acetone	C_3	H_3	O
1 at. metacetone	C_6	H_5	O
3 at. carbonic acid		C_3	O_6
1 at. water		H	O
1 at. anhydrous sugar	C_{12}	H_9	O_9

PRODUCTS OF THE OXIDATION OF SUGAR.

Saccharic Acid. — Formula, $C_{12}H_5O_{11}+5HO=C_{12}H_{10}O_{16}$. (Thaulow.) It is a product of the action of dilute nitric acid on cane or grape sugar. Scheele confounded it with malic acid. More lately Guérin Varry described it as oxalhydric acid; and it has been specially investigated by Erdmann, Hess, and Thaulow.

To obtain this acid, 1 part of sugar or gum is dissolved with the aid of heat in 2 parts of nitric acid diluted with 10 of water, and heat is applied as long as reaction takes place. After neutralizing the liquid by carbonate of lime, neutral acetate of lead is added. An abundant white precipitate is formed, which is decomposed by sulphuretted hydrogen. The acid liquid thus obtained is half neutralized with potash, and evaporated in the water-bath. After sufficient concentration, the liquid, if set aside, deposits crystals of acid saccharate of potash, which are decolorized by animal charcoal. The decolorized liquid is again crystallized, the crystals redissolved, reprecipitated by acetate of lead; and the precipitate, again decomposed by sulphuretted hydrogen, yields pure saccharic acid.

The diluted acid is a colourless slightly acid liquid; when concentrated it is syrupy, colourless, strongly acid, and by long standing it deposits colourless crystals. (Guérin.)

It forms flocculent white precipitates in lime and barytic water, which disappear on adding an excess of acid. It does not precipitate the salts of lime or baryta, nor even the nitrate of silver, until ammonia is added, when it forms a white precipitate which is reduced by the slightest heat. The metallic silver, as there is no effervescence, attaches itself to the surface of the vessel, forming a bright mirror-like coating. Nitric acid, with the aid of heat, converts it into oxalic and carbonic acids. Heated with superoxide of manganese and sulphuric acid, it yields formic acid. Alkaline solutions added in excess, and heated with saccharic acid, give it a deep brown colour. It is soluble in alcohol in all proportions, not in ether. It dissolves zinc and iron, with disengagement of hydrogen. When kept in the diluted state it becomes mouldy.

Salts of Saccharic Acid.—This acid is very remarkable for the large number of compounds it forms with bases. It forms five series of salts, according as 1, 2, 3, 4 or 5 atoms of basic water contained in it are replaced by their equivalents of metallic oxides. The following table contains the saccharates, the composition of which is known :—

$C_{12}H_5O_{11} + 5HO$	hydrated acid.
$C_{12}H_5O_{11} + \left.\begin{matrix}KO\\4HO\end{matrix}\right\}$	acid salt of potash.
$C_{12}H_5O_{11} + \left.\begin{matrix}4HO\\AdH_2O\end{matrix}\right\}$	acid salt of ammonia.
$C_{12}H_5O_{11} + \left.\begin{matrix}2PbO\\3HO\end{matrix}\right\}$	first salt of lead.
$C_{12}H_5O_{11} + \left.\begin{matrix}2ZnO\\3HO\end{matrix}\right\}$	salt of zinc.
$C_{12}H_5O_{11} + \left.\begin{matrix}3PbO\\2HO\end{matrix}\right\}$	second salt of lead.
$C_{12}H_5O_{11} + 5PbO$	third salt of lead.

If we add the elements of the basic water to those of the anhydrous acid, we find that the saccharic acid contains the elements of 1 atom of mucic acid, $C_{12}H_8O_{14} + 2HO = C_{12}H_{10}O_{16}$; that the first salt of lead and the salt of zinc have a composition identical, as far as the acid is concerned, with that of the mucate of silver, $C_{12}H_8O_{14} + 2PbO = 2(C_6H_4O_7 + AgO)$, that is, the acids in these salts are isomeric or polymeric; and finally, that in the third salt of lead the saccharic acid has the same composition as the citric acid in the citrate of silver; only the latter is combined with three atoms of base instead of five.

The production of two isomeric (or polymeric) acids, the saccharic and mucic, by the oxidation of two different substances, cane sugar and sugar of milk, which by fermentation yield the same products, appears likely to lead to the solution of the important problem which is still to be solved in regard to the constitution of these bodies, as well as of others, such as gum and starch, of which we hardly know more than the relative proportions of their elements.

The saccharates, although of the highest importance in reference to the theory of acids and salts, have little interest individually in their properties, and need not here be described in detail. The existence of the third salt of lead above described, $C_{12}H_5O_{11} + 5PbO$, is one of the most convincing proofs of the existence of acids requiring more than one atom of base to form neutral salts. The oxide of lead here cannot be less than 5 atoms; because, if we reckon it 1, 2, 3 or 4, we shall have fractions of atoms in the composition of the acid. When, moreover, we observe in the two other salts of lead, that, for every atom of oxide of lead present, an atom of water has been eliminated, we cannot hesitate in considering the saccharic acid as a polybasic acid (quinquebasic). To deny this would lead to the admission of a different acid in each of the three salts of lead, and another in the salt of potash.

REMARKS ON THE CONSTITUTION OF THE COMPOUNDS OF THE DIFFERENT KINDS OF SUGAR, AND THE PRODUCTS OF THEIR DECOMPOSITION.

Notwithstanding the great analogy between cane sugar and grape sugar, both in their taste and in the properties of many of the products of their decomposition, we have only to consider their chemical characters to be convinced that they are as distinct from each other as, for example, starch and woody fibre are from grape sugar.

Thus the strong mineral acids, which hardly act on grape sugar, destroy cane sugar with facility; grape sugar, on the other hand, is instantly destroyed by alkalies; while cane sugar forms with lime, baryta, and oxide of lead, compounds of uniform composition which are permanent in the dry state.

Grape sugar produces, by the action of alkalies, a totally different series of compounds from those formed by cane sugar under the same circumstances. (Braconnot.) The phenomena which they exhibit in reference to polarized light are also quite different. (Biot.)

If they only differed by the amount of water contained in them in the hydratic state, their composition in the anhydrous state being the same, there would be no means of explaining such differences: moreover, if this were the case, it ought to be as easy to convert grape sugar into cane sugar, as to do the reverse. In fact, however, these substances have nothing in common except the sweet taste, a property which they share with many other substances; the property of forming a definite compound with chloride of sodium; and finally, the property of fermenting under certain circumstances, giving rise to the same products. But there is good reason to believe that cane sugar does not ferment till it has been converted into grape sugar.

The following table gives a view of the chief products of cane sugar and grape sugar:—

$C_{12}H_9O_9 + 2HO$ = cane sugar.
$C_{12}H_9O_9$ = caramel.
$C_{12}H_9O_{15}$ = saccharic acid, in the salt of potash.
$C_{12}H_8O_{14}$ = ditto, in the salt of zinc.
$C_{12}H_7O_{13}$ = ditto, in the second salt of lead.
$C_{12}H_5O_{11}$ = ditto, in the third salt of lead.
$2\frac{1}{2}(C_{12}H_6O_6)$ = sacchulmic acid.
$C_{12}H_8O_8 + 3HO$ = glucic acid.
$2(C_{12}H_5O_4) + HO$ = brown matter formed by hydrochloric acid from cane sugar. (Stein.)
$2(C_{12}H_6O_5)$ = melassic acid.

This table shows that 7 atoms of anhydrous sugar contain the elements of 1 atom of saccharic acid, 3 atoms of melassic acid, and 17 atoms of water; and that 2 atoms of saccharic acid contain the elements of 1 atom of melassic acid, 10 atoms of formic acid, and 4 atoms of oxalic acid. These considerations may help to explain the formation of melassic acid. At all events, it is not uninteresting to observe that saccharic acid contains the same number of atoms of carbon as sugar does, and seems to be formed from sugar as acetic acid is from alcohol.

When we compare the properties of the sugars above described with the processes followed in preparing them, we naturally conclude that such vegetable juices as contain free acids do not yield cane sugar when boiled or evaporated, but rather grape sugar, or uncrystallizable compounds of grape sugar with organic acids. Now cane sugar is converted into grape sugar by contact with sulphuric acid; and still more rapidly if heated with it. Again, the grape sugar, the formation of which cannot be prevented in the liquids from which cane sugar is extracted, is rapidly converted into glucic or melassic acid during the clarification of the juice by lime.

By the formation of glucic acid, 1 eq. of sugar disappears for each eq. of lime, and the molasses then contain glucate of lime. The juice of beetroot contains sea-salt and oxalate of potash. The sea-salt, in uniting with cane sugar, forms a compound which is deliquescent, and contains 6 parts of sugar for 1 of sea-salt; it remains in the mother-liquid as an uncrystallizable syrup. The lime decomposes the oxalate of potash; and the free potash, which the concentrated syrup now contains, converts part of the sugar with the aid of heat into melassic acid, which gives the syrup its brown colour.

Several manufacturers have proposed to neutralize the free alkali with sulphuric acid after the clarification by the milk of lime. This operation (Kodweiss, Ann. der Pharm.) agrees perfectly with theory, and has been confirmed by long experience.

SUGAR OF MILK, OR LACTINE.

Formula, $C_{24}H_{24}O_{24}$ or $C_{24}H_{19}O_{19} + 5HO$. (Berzelius.) Dried at 300°, $C_{24}H_{19}O_{19}$. (Berzelius.) Dried at 248°, $C_{24}H_{19}O_{19} + 3HO$. Formulæ of its compounds with oxide of lead, $C_{24}H_{19}O_{19} + 5PbO$ and $C_{24}H_{19}O_{19} + 10PbO$.

Bartholdi first described sugar of milk in 1619; up to the present time it has only been found in the milk of the mammalia.

It is obtained pure by evaporating whey till it crystallizes, and treating the crystals with animal charcoal, and repeated crystallizations.

Sugar of milk crystallizes from its aqueous solutions in parallelopipeds, terminated by four-sided pyramids, which are white, semi-transparent, hard, crackling in the teeth, and assuming a foliated structure. Their sp. g. is 1·543; they dissolve in 5 or 6 parts of cold water, and in 2½ parts of boiling water, without forming a syrup. The crystals have a very feeble sweet taste, but the taste of a concentrated solution is much more decided.

When gently heated, first to 248°, and then to 284°, the crystals lose, without melting, 2 at. water, = 5·3 p. c.; but, if heated rapidly, they melt and lose 12·4 p. c. = 5 atoms of water. At 300°, the melted liquid begins to turn yellow. (Berzelius.)

Sugar of milk is permanent in the air, loses no weight at 212°, and is insoluble in alcohol and ether. It is more soluble in acid and alkaline liquids than in pure water; it does not precipitate metallic solutions, and is not precipitated by infusion of galls.

Dilute mineral acids, such as sulphuric acid, or hydrochloric acid, convert sugar of milk, by a prolonged contact in the cold, and still more rapidly by boiling, into grape sugar. According to Vogel, the weight of the grape sugar produced is rather less than that of the sugar of milk employed. By calculation, 100 parts of sugar of milk, by combining with 2 at. of water, should produce 109·8 parts of grape sugar. The strong mineral acids, in acting on sugar of milk, produce the same substances, sacchulmine and sacchulmic acid, as are produced by cane sugar. When triturated with slaked lime and water, sugar of milk is dissolved with production of heat, and forms a brown liquid, from which alcohol precipitates a thick, bitter syrup, which attracts moisture from the air, and precipitates metallic solutions (Bouillon-Lagrange and Vogel); the alcohol dissolves acetate of potash. The relations between this liquid, sugar of milk, and glucic acid, have not been ascertained.

Nitric acid, with the aid of heat, converts sugar of milk into mucic acid; a part of this acid always passes into oxalic acid in the operation.

With the oxides of metals easily reducible, sugar of milk acts just as cane and grape sugar do. The higher degrees of oxidation are reduced to protoxides or to the metallic state, while formic acid is produced.

The presence of sugar of milk in metallic solutions prevents the precipitation of the oxides by alkalies in many cases.

An aqueous solution of arsenic acid, when mixed with a solution of sugar of milk, acquires a reddish-brown colour after a short time.

Powdered sugar of milk absorbs ammoniacal gas (Berzelius), and hydrochloric acid (Bouillon-Lagrange and Vogel). It also combines with oxide of lead.

When milk is exposed to a temperature of from 95° to 104°, it undergoes the vinous fermentation; the sugar disappears, and alcohol is found in the liquid, while carbonic acid is disengaged during the whole fermentation. It is probable, however, that, before fermenting, the sugar of milk is converted into grape sugar, for the fermentation does not begin till the milk has curdled, that is, till an acid has been formed; and this acid may be the cause of the conversion of the sugar of milk into grape sugar. It has long been known that the curd of milk causes grape sugar to ferment. Since, therefore, the sugar of milk agrees with cane sugar in not fermenting until it has been converted into grape sugar, it has been thought advisable to describe it along with cane and grape sugar, the principal characters of which it possesses.

Sugar of Milk and Oxide of Lead.—A solution of sugar of milk, mixed with oxide of lead, becomes brown when boiled; but when the temperature does not exceed 140°, it remains colourless, and contains three different compounds. There is deposited at the bottom of the vessel a heavy granular powder, which becomes yellow and dried, and contains 87·2 p. c. = 10 at. oxide of lead. This is the basic compound. The liquid retains in suspension a white viscid compound, which, when dried, becomes yellowish and semi-transparent. It contains 63·729 p. c. = 5 at. oxide of lead, and is the neutral compound. Finally, the filtered liquid yields, on the addition of ammonia, an additional quantity of the neutral compound; and the liquid, evaporated to dryness, produces a transparent gummy mass, also becoming yellow when dried, and containing 18·12 p. c. oxide of lead. (Berzelius.)

PRODUCTS OF THE OXIDATION OF SUGAR OF MILK.

Mucic Acid. — Formula, $C_{12}H_8O_{14} + 2HO$. (Berzelius, Malaguti.) Symbol, $\bar{M} + 2$ aq. This acid was discovered by Scheele. It is formed by the action of dilute nitric acid on sugar of milk, gum, picromel, or mannite. One atom of crystallized sugar of milk, by taking up 12 at. oxygen, and losing 4 at. water, produces 2 at. crystallized mucic acid.

To obtain it, 1 part of gum or of sugar of milk is dissolved in 4 parts of nitric acid, sp. g. 1·42, diluted with 1 part of water. Heat is applied till all effervescence has ceased; and, on cooling, the mucic acid is deposited. The acid from sugar of milk is always pure, while that from gum always contains mucate of lime, which is removed by neutralizing with an alkali and precipitating by an acid.

Mucic acid forms a white crystalline powder, which crackles in the teeth; its taste is feebly acid. It is soluble in 6 parts of boiling water, insoluble in alcohol, and very sparingly soluble in diluted acids. Its aqueous solution reddens litmus.

Mucic acid dissolves in oil of vitriol, giving to it a crimson colour. When this solution is heated, it is charred. It is probable that in the first instance a compound of the two acids is formed; for, on neutralizing the mixture with baryta, a considerable quantity of that base remains in solution. When the aqueous solution of mucic acid is evaporated by prolonged ebullition, the acid passes into the state of *modified mucic acid.*

When subjected to dry distillation, mucic acid blackens; and produces, among other substances, *pyromucic acid.*

SALTS OF MUCIC ACID.

Mucic acid neutralizes 2 equivalents of base, which are represented by 2 equivalents of a metallic oxide, or 1 eq. metallic oxide and 1 eq. water.

The alkaline mucates are soluble in water; those of the alkaline earths or of the heavy metallic oxides are insoluble. They are all decomposed by the mineral acids, which seize the base, and set free the mucic acid.

The mucate of silver contains 2 eq. oxide of silver, and forms a gelatinous precipitate. The formula of the mucate of lead is $\bar{M},2PbO + 2$ aq.

With potash and soda, mucic acid forms two kinds of salt: in one series, 1 atom of basic water is replaced by 1 atom of alkali; in the other, 2 at. basic water are replaced by 2 at. alkali. The composition of these salts, however, is little known.

Mucate of Ammonia.—Formula, $\bar{M},2AdH_4O$. It is prepared by supersaturating with carbonate of ammonia a hot solution of mucic acid. It crystallizes on cooling in flattened parallelopipeds, which are not decomposed by a new crystallization. This salt does not lose ammonia at 230°. (Malaguti.)

Mucate of Oxide of Ethule.—Formula, $\bar{M},2AeO$. (Malaguti.) To prepare it, 1 part of mucic acid is dissolved in 4 parts of oil of vitriol with the aid of a gentle heat, and the solution allowed to cool. When it has become black, 4 parts of alcohol, sp. g. 0·814, are added, and the mixture left to itself for twenty-four hours. During this time, it forms a white semi-solid mass, impregnated with a black acid liquid; the whole is placed on a porous brick and allowed to dry. The dry crystals are purified by solution in alcohol and recrystallization.

The mucate of oxide of ethule crystallizes in four-sided prisms, colourless and semi-transparent. Their sp. g. is 1·17. They melt at 316°, and solidify again at 275°. At 338° they are resolved into alcohol, carbonic acid, acetic acid, pyromucic acid, and a residue of carbon. These crystals are sparingly soluble in cold water, but very soluble in boiling water; the solution has a bitter taste, and on cooling deposits rhombic prisms of the sp. g. 1·32, melting at 316° and solidifying at 250°. These prisms are soluble in 2·27 parts of cold water, in 155 parts of cold alcohol, and more easily in hot water and alcohol. They are insoluble in ether.

The solution in water of mucate of oxide of ethule is decomposed by boiling, especially when an alkaline base is added. The products of this decomposition are alcohol and mucic acid; the latter unites with the base.

Dry ammoniacal gas exercises no sensible action on the mucate of oxide of ethule at temperatures below 338°; but, if distilled in a current of ammonia, there is formed a very aromatic oil which dissolves in water, giving it a yellow colour. When this product is gently heated in a current of chlorine, it is converted into a yellow uncrystallized mass, very soluble in alcohol.

Modified Mucic Acid.—Laugier has observed that mucic acid acquires very different properties when its concentrated aqueous solution is boiled, or evaporated at a high temperature. It then leaves a residue slightly coloured, having much stronger acid properties than the mucic acid itself. This modified acid is much more soluble in cold water; it is soluble in alcohol, and it forms salts which have different external characters from those of the mucates. By the spontaneous evaporation of its alcoholic solution it is obtained in square tables.

It is soluble in 17·2 parts of boiling water, and in 73 parts of cold water. When its boiling saturated solution is allowed to cool, it deposits crystals of ordinary mucic acid. Its salts are more soluble than those of the unaltered mucic acid. It is easily converted into ordinary mucic acid when dissolved in water, whether alone or in combination with bases.

When a saturated hot solution of modified mucic acid is saturated with ammonia, there is precipitated an insoluble salt containing the modified acid; while mucic acid, in the same circumstances, does not deposit crystals for some time. The modified acid, when distilled, yields the same products as the ordinary mucic acid.

Malaguti found both acids to contain equal proportions of the same elements. But the salt formed with oxide of silver by the modified acid yielded less silver than the mucate. The atomic weight of mucic acid is 1208·546, while that given by experiment for the modified acid is 1329, or 1320; this would indicate that the latter contained the elements of 1 atom of water more than the former. But as this salt of silver was not analyzed so as to ascertain the composition of the acid it contained, the question of the identity in composition of the two acids remains for the present undecided.

Pyromucic Acid.—Formula, $C_{10}H_3O_5 + HO$. Symbol, $p\overline{M} + aq.$ (Boussingault, Malaguti, Pelouze.) This acid was discovered by Scheele, who confounded it with benzoic acid. It is formed by the dry distillation of mucic acid. One at. mucic acid contains the elements of 1 at. pyromucic acid, 6 at. water, and 2 at. carbonic acid. $C_{12}H_8O_{14} + 2HO = C_{10}H_3O_5 + HO + 2CO_2 + 6HO$. To prepare it, the solid and liquid products of the distillation of mucic acid are first dried in the water-bath, and then sublimed at a temperature of from 265° to 284°. The yellowish sublimate is purified by solution and recrystallization in water. It forms elongated tables, white and brilliant, melting at 265°, and subliming without residue at a temperature a little higher. It condenses in yellowish oily drops, which, on cooling, form a crystalline mass. It is permanent in the air, soluble in 26 parts of cold water, and in 4 parts of boiling water. The acid crystallized from water closely resembles benzoic acid, from which, however, it is distinguished by its greater solubility in cold water. It is easily soluble in alcohol, and is not changed by nitric acid.

In its combinations with bases, its basic water is replaced by 1 eq. of base. The pyromucates of oxide of ethule, of baryta, and of silver are anhydrous. All the neutral pyromucates with metallic base are soluble in water. The alkaline pyromucates are very soluble. Some of them are also soluble in alcohol. The rest are less soluble and crystallizable. Subacetate of lead is precipitated by pyromucic acid.

Pyromucate of Oxide of Ethule.—Formula, $AeO,p\overline{M}$. Discovered and analyzed by Malaguti. It is obtained by distilling a mixture of 10 parts of pyromucic acid, 20 parts of alcohol, sp. g. 0·814, and 5 parts of concentrated hydrochloric acid. The product is returned into the retort and redistilled five times, and is then mixed with water; the new compound then separates in oily drops, which soon form a crystalline mass. The crystals are washed with water, and, after being dried, they are again distilled. The product which passes over at the end of the distillation is pure and anhydrous. It crystallizes in plates of four, six, and eight sides, derived from a rhomboidal prism, colourless, transparent, and unctuous to the touch. It has an odour like that of benzoic ether and also like naphthaline, and a pungent bitter taste, with an agreeable after-taste of anise and camphor. Its sp. g. is 1·297; it melts at 94°, and boils between 406° and 412°. The density of its vapour is 4·859, representing four volumes. Calculation gives $\frac{19 \cdot 455}{4} =$ 4·863. It is sparingly soluble in water, soluble in alcohol and ether in all proportions. It does not inflame by contact with a burning body. By keeping, it gradually becomes coloured: ammonia does not change it, the fixed alkalies decompose it. The strong mineral acids dissolve it in the cold without change, but decompose it with the aid of heat.

In contact with chlorine gas, this body undergoes a peculiar change. It melts with disengagement of heat, without the production of hydrochloric acid or other gaseous products, and is found after the operation to have doubled its weight. When all excess of chlorine has been removed, there is obtained a colourless syrupy liquid, of a strong aromatic odour and a persistent bitter taste. Its sp. g. is 1·496, and it is neutral to the test paper. When heated, it blackens, and gives off hydrochloric acid. It is very soluble in alcohol and ether. In water and in a moist air it becomes opaque and milky, being decomposed with formation of hydrochloric acid. This substance, which Malaguti, who discovered it, calls *Chloropyromucic Ether*, becomes hot when placed in contact with caustic potash; it then acquires colour, and deposits a curdy mass, which, with the aid of heat, is dissolved by the water. In this reaction the solution gives off vapours of alcohol; it becomes reddish-brown, and contains much chloride of potassium, but no pyromucic acid. When the chloropyromucic ether is mixed with alcohol previously saturated with ammonia, it blackens, and is converted into sal-ammoniac and hydrocyanate of ammonia. Pyromucate of oxide of ethule absorbs 4 eq. of chlorine to form the new ether, the empirical formula of which is $C_{14}H_8O_6Cl_4$. (Malaguti.) We have no positive data as to the arrangement of the elements in this compound; it appears, however, from the action of alkalies upon it, and the production of alcohol attending that reaction, that it is not the oxide of ethule, but the pyromucic acid, which is acted on by the chlorine. According to Berzelius, it may be viewed as a mixture of pyroracemate of oxide of ethule with subchloride of carbon, thus,

$$C_4H_5O,\ C_6H_3O_5,\ C_4Cl_4.$$

But the latest experiments of Malaguti do not confirm the constitution expressed by this formula.

MUSHROOM SUGAR.

By acting on the alcoholic extract of ergot of rye with water, Wiggers obtained a saccharine liquor, which, when evaporated to a syrup, yields quadrangular prisms, with a rhombic base, terminated by dihedral summits, colourless, transparent, soluble in water and alcohol, insoluble in ether. This substance, in contact with yeast, undergoes the vinous fermentation. When the crystals are heated, they melt, and by a stronger heat are charred, giving out the odour of caramel. Nitric acid with the aid of heat converts them into oxalic acid.

When boiled with acetate of copper, this sugar does not precipitate any protoxide of copper: this is the only property by which it is distinguished from the other kinds of sugar.

Pelouze and Liebig, by the analysis of a small portion, not perfectly pure, obtained 38·3487 p. c. of carbon, and oxygen and hydrogen in the proportions to form water. These results are expressed exactly by the formula $C_{12}H_{13}O_{13}$; that is, the composition of grape sugar, minus 1 at. of water.

The substance described by Braconnot under the name of mushroom sugar is *mannite*, a substance which will shortly be described.

TASTELESS SUGAR.

In the sixth edition of his "Traité de Chimie," vol. iv. p. 351, Thénard states, that, by evaporating the urine of patients affected with *diabetes insipidus*, he has several times obtained, instead of grape sugar, a considerable quantity of crystals, which were tasteless, or had a very faint sweetish taste. This observation has lately been confirmed by Bouchardat.

This tasteless sugar, in contact with ferment, undergoes the vinous fermentation. When boiled with one-tenth of sulphuric acid, and a sufficient quantity of water, it acquires the taste of grape sugar, with which it agrees in form and solubility. This substance merits a careful investigation.

REMARKS ON THE NATURAL STATE AND FORMATION OF THE DIFFERENT SPECIES OF SUGAR.

Under the head of grape sugar we have mentioned several processes which prove that woody fibre and starch may be transformed into sugar, when subjected to the action of acids under certain conditions; we have further shown that sugar is produced by the contact of starch with malt; and lastly, we have seen that salicine and phloridzine, by the action of acids, also yield grape sugar.

In like manner, amygdaline, under the influence of the white albuminous matter contained both in sweet and bitter almonds, and which has been called emulsine, is decomposed into several products, one of which is sugar.

The active principle in malt, which produces the remarkable transformation of starch into grape sugar, is a substance which is not volatile, contains nitrogen, is tasteless, colourless, soluble in water, neutral to test paper, to which Payen and Persoz have given the name of *Diastase*. One part of diastase is sufficient to convert, in a few hours, 2000 parts of starch into sugar, provided the temperature do not exceed 158°. Diastase combines with no other substance; it is insoluble in absolute alcohol, soluble in weak alcohol. To obtain it, malt of the best quality is moistened and subjected to pressure; the juice is mixed with a little alcohol, which separates foreign matters, such as albumen; the filtered liquid contains diastase in solution.

In proportion as the diastase acts on starch, converting it into sugar, it disappears itself; and when the solution no longer acts on a fresh portion of starch, the presence of diastase cannot be detected in it. The reaction consequently is a purely chemical one, the careful study of which must certainly throw light on a multitude of the phenomena of vegetation.

The sugar formed during the germination of seeds containing starch, by the action of diastase, disappears at the same time that the woody fibre, forming the skeleton of the young plant, is developed.

Woody fibre (or lignine), and sugar, differ from one another, for the same quantity of carbon, only in the proportion of the elements of water. For 12 atoms of carbon, anhydrous sugar contains 9 atoms, woody fibre 8 atoms, of water.

Woody fibre may be converted into grape sugar by the action of sulphuric acid; now, an inverse transformation seems to take place during the maturation of pulpy fruits, such as apples and pears, &c., as well as during the developement of the germs of plants. In fact, previous to maturity, fruits are formed of a compact cellular tissue containing the elements of woody fibre, and filled with a liquid, containing very little sugar, a gummy substance, and a large quantity of free acid. During maturation, a part of the acid disappears by the influence of the oxygen of the air; the cellular tissue diminishes, and the proportion of sugar increases, insomuch that, instead of hard, woody, acid fruits, we obtain, if the maturation have been complete, some weeks after they have been gathered, fruits which yield a sweet and syrupy juice, contained in a coriaceous envelope.

The shoots of asparagus, as long as they have not risen above the surface of the soil, contain a large quantity of sugar; when acted on by light, they become green, and, as the colour deepens, the sugar disappears.

OF THE ALCOHOLIC OR VINOUS FERMENTATION.

This name is given to the peculiar decomposition which the different species of sugar undergo in certain circumstances; and by which their elements combine to form new compounds, which, under similar conditions, are always the same.

When a saccharine solution is placed in contact with substances in a state of decomposition or putrefaction, it is observed, after about twenty-four hours, if the temperature be kept between 38° and 86°, that the taste of the sugar has disappeared; pure carbonic acid is disengaged, and the liquid has acquired intoxicating properties. It now contains alcohol, which may be separated by distillation. If we compare the composition and quantity of these products with that of the sugar employed, we shall find them to contain the same weight of carbon.

Grape sugar, dried at 212°, contains the elements of 4 at. carbonic acid and 2 at. alcohol.

$$\begin{array}{l}
C_4 \qquad O_8 = \text{4 at. carbonic acid.} \\
C_8\,H_{12}\,O_4 = \text{2 at. alcohol.} \\
\hline
C_{12}H_{12}\,O_{12} = \text{1 at. grape sugar, dried at 212°.}
\end{array}$$

Hence, in fermentation, 1 atom of crystallized grape sugar, = $C_{12}H_{14}O_{14}$, must lose 2 at. water, and 100 parts of this sugar must yield 44·84 parts carbonic acid, 47·12 parts alcohol, and 9·04 parts water. Guérin-Varry obtained, in two experiments, 10·572 of carbonic acid to 11·071 of alcohol, and 10·632 of carbonic acid to 11·166 of alcohol. The first experiment gives, for 44·84 of carbonic acid, 46·95 of alcohol: the second gives, for the same quantity of carbonic acid, 47·09 of alcohol. It follows from these results that, in fermentation, sugar produces these new substances by a new grouping of its elements, without the elements of the body which excites the fermentation taking any share in the transformation.

According to the formula which we have adopted for crystallized cane sugar, that substance contains the elements of 4 at. carbonic acid, 2 at. oxide of ethule, and 1 at. water; there are consequently required the elements of 1 at. water to enable it to yield the same products as 1 atom of dried grape sugar.

Very exact experiments have shown that 100 parts of cane sugar give from 50·3 to 51·27 parts of carbonic acid, and 52·62 parts of alcohol. The sum of these products amounts to 103·89, that is, to more than the weight of the sugar fermented. This excess is found in the alcohol formed, as oxygen and hydrogen, in the proportions to form water. It is, therefore, certain that in the fermentation of cane sugar, the elements of 1 at. water have a share in the transformation. One hundred parts of cane sugar and 5·025 parts of water ($C_{12}H_{11}O_{11} + HO$) produce, after fermentation,

51·298 carbonic acid,
and 53·727 alcohol.
105·025

Fermentation is nothing else but the putrefaction of a substance containing no nitrogen; that is to say, a metamorphosis by which the elements of a complex molecule group themselves, so as to form more intimate and more stable compounds, according to the special attractions of these elements. It is excited by the contact of all bodies, the elements of which are in a state of active decomposition. In nitrogenized substances of a very complex constitution, putrefaction (or fermentation) is spontaneously established when water is present, and when the temperature is sufficiently high, and it continues till the original compounds are wholly destroyed. Substances containing no nitrogen, on the contrary, require, in order to their undergoing this metamorphosis, the presence of a nitrogenized substance, already in a state of putrefaction (fermentation). The substances which best promote the change are gliadine, gluten, vegetable albumen, in short, all substances in a state of spontaneous decomposition to which the general name of *ferment* is given. Putrefying animal substances are equally capable of exciting the same action.

Fermentation or putrefaction occurs only in complex organic molecules, of a higher order. The reactions of these substances, with the ordinary chemical agents, show that the force which retains their elements in a state of combination is extremely feeble. Every substance which acts on them tends to cause their elements to assume a new arrangement, so that new products are formed, which, even in the same kind of decomposition, differ from each other. We may assume that the molecules of the class of compounds to which the sugars belong are only retained in combination by virtue of the *vis inertiæ* of their elements, and that every change in the equilibrium of these elements forces them to attract each other in a different order. Among the causes which disturb this equilibrium we must place the influence which a body undergoing spontaneous decomposition exercises on another compound susceptible of the same kind of decomposition.

Ferment, or yeast, is a substance in a state of putrefaction, the atoms of which are in a continual motion.

This motion, or conflict of the elements, communicating itself to the sugar, destroys the equilibrium of its atoms. These no longer retain the same arrangement, and group themselves according to their special attractions. The carbon of the sugar is divided between the hydrogen and the oxygen: there is formed, on the one hand, a carbonized compound, containing almost all the oxygen (carbonic acid); and on the other, a second carbonized compound, containing all the hydrogen (alcohol). This kind of decomposition is the same for all organic substances which putrefy, or undergo a metamorphosis; it being understood that the products vary according to the composition of these substances.

It is highly probable that cane sugar, before it undergoes the vinous fermentation, is converted into grape sugar by contact with the ferment; and that consequently it is grape sugar alone which yields alcohol and carbonic acid.

We have classed lactine with the sugars, on account of the indisputable fact, that this substance disappears in milk exposed to a proper temperature with the same phenomena as characterize the fermentation of the other sugars. In this case, also, carbonic acid is disengaged, and alcohol left in the liquid.

It is therefore probable, if not certain, that the lactine is converted into grape sugar, before giving rise to these products; for milk does not ferment until it be sour, and, when the fermentation is over, there is found in the liquid a large quantity of an organic acid. Now, we know that lactine, by the action of many acids, is converted into grape sugar; and it is natural to conclude that the same transformation occurs before, or during, the fermentation of milk.

In the fermentation of vegetable juices containing sugar, it appears that the elements of certain other principles therein dissolved take an essential part in the formation of the new products occasioned by the action of the air on the juice of the grape, of fruits, and of other plants.

The nitrogenized matters in solution, such as gluten, gliadine, vegetable albumen, &c. are spontaneously decomposed; and it is then that the decomposition of the sugar is commenced, and continues alone till the sugar has entirely disappeared. When the juice has once begun to ferment, it may be preserved from the contact of the atmosphere, without the action being thereby arrested. The nitrogenized matters of the juice are constantly precipitated in the shape of ferment or yeast; and in the fermented liquors, besides alcohol, there are found other substances, such as œnanthic ether, oil of potatoe, oil of grain, &c. the presence of which could not be detected previous to fermentation. These latter are probably the products of the action of the nitrogenized matters of the juices on the sugar they contained.

With regard to the phenomenon commonly termed viscous or mucilaginous fermentation, it is certainly the result of the reciprocal action of the substances held in solution in the vegetable juices. Mannite and lactic acid are the principal products of this reaction.

OF THE VISCOUS FERMENTATION.

When the juice of beet-root, of carrots, of onions, and other saccharine vegetables, is exposed to a temperature of from 86° to 104°, a brisk effervescence is observed; cane sugar is transformed into grape sugar, carbonic acid is disengaged, and when the action is over, all the sugar has disappeared. The liquid contains merely traces of alcohol; but, on the other hand, a large quantity of mannite and of lactic acid. Besides these, there is found a substance which is precipitated by alcohol in the shape of a syrupy mucilage, (hence the term viscous or mucilaginous fermentation,) very thick, and possessing exactly the composition of gum arabic. All these substances seem to be the result of the action of the nitrogenized or albuminous principles of the juice on the sugar. With the exception of ammonia, no other nitrogenized substance can be discovered in the fermented liquor. Now, gum arabic, or a substance of the same composition, contains exactly the elements of cane sugar; and mannite, *plus* lactic acid, contains the elements of dried grape sugar, minus 1 at. oxygen.

$$\begin{array}{ll} \text{Mannite} & = C_6\ H_7\ O_6 \\ \text{Lactic acid} & = \underline{C_6\ H_5\ O_5} \\ & \quad C_{12}\ H_{12}\ O_{11} \end{array}$$

It is, therefore, possible that these two substances are formed by a deoxidation of sugar, 1 at. of oxygen from which combines with the elements of the nitrogenized substances.

To excite the viscous fermentation in pure sugar, it is dissolved in 20 parts of water, which has previously been boiled with the yeast of beer free from starch, or with gluten; the solution is then left in a temperature of 86° to 104°. (Desfosses, Pelouze.) Sulphuric acid, infusion of nut-galls, and many other substances prevent this decomposition.

On account of the connection of lactic acid and mannite with sugar, the history of these substances is here subjoined.

MANNITE.

Formula, $C_6H_7O_6$. It is named from Manna, of which it forms the greater part. It is also found in the juices which exude from several species of cherry and apple, in various mushrooms, in some roots, such as that of celery; in the fermented juice of beet-root, carrots, onions, &c.; and it is also obtained in small quantity when starch is transformed into grape sugar by boiling with diluted sulphuric acid. It is easily purified by solution in boiling alcohol, which on cooling deposits almost the whole of it in fine radiated groups of crystals. These are quadrangular prisms, anhydrous, colourless, transparent, of a silky lustre. From water it crystallizes in very large anhydrous prisms. It has a faint sweetish taste, is very soluble in water and in hot alcohol, sparingly soluble in cold alcohol. Its aqueous solution cannot be made to undergo the vinous fermentation.

Mannite melts without loss of weight, into a colourless liquid, which, on cooling, forms a crystalline mass. Nitric acid converts it into oxalic and saccharic acids, not into mucic acid. Hypermanganate of potash converts it into oxalate of potash. Concentrated arsenic acid gives it a brick-red colour. Its aqueous solution dissolves oxide of lead.

LACTIC ACID.

Formula of the acid in the lactate of zinc, $C_6H_5O_5$. Symbol $\bar{L}$; hydrated acid, $C_6H_5O_5 + aq. = \bar{L}, aq.$; sublimed acid $C_6H_4O_4$.

Lactic acid was discovered by Scheele in whey. Braconnot also described it under the name of Nancéic acid. It was found by Berzelius in several animal liquids, and particularly in human urine. (Henry.) It is formed in milk when it becomes sour, in the fermentation of several vegetable juices, and in the putrefaction of some animal matters. The acid which is found in the fermented juice of beet-root, turnips, and carrots, in sour-krout, in fermented rice-water, in the fermented extract of nux vomica, and in the infusion of bark used by tanners, is for the most part pure lactic acid.

To obtain lactic acid, the lactate of baryta is dissolved in water, and the baryta separated by dilute sulphuric acid, avoiding excess. The liquid filtered from the sulphate of baryta is evaporated in vacuo along with sulphuric acid, assisting the evaporation with a gentle heat. In this way is obtained the hydrated acid, which is further purified by being dissolved in ether, the solution filtered, and the ether removed by evaporation.

The hydrated lactic acid is a colourless syrupy liquid; its sp. g. is 1·215 at 68°. It has a very strong acid taste, which is remarkably weakened by diluting the acid. It attracts moisture from the air. At 480° it is decomposed. The most remarkable product is a crystalline sublimate, which has been called *sublimed* or *concrete lactic acid*. The greater part of the acid is converted into this new body, which sublimes in shining white crystals: they are purified by pressure in bibulous paper, and solution in boiling alcohol. On cooling, the new acid is deposited in rhomboidal tables of dazzling whiteness, fusible at 225°, volatile at 480°, yielding white, inflammable, acrid vapours. These crystals have a weak acid taste, dissolve slowly in cold water, but are quickly dissolved in hot water, and attract moisture from the air. The solution yields, by evaporation, a thick syrup, which has all the properties as well as the composition of the hydrated acid above described. No crystals can be obtained from this solution. That which is most remarkable in this body is its composition, which is expressed by the formula $C_6H_4O_4$; it is, therefore, distinguished from the hydrated acid by containing 2 at. of water less, which sufficiently explains its mode of formation. The conversion of its solution, moreover, into hydrated acid by evaporation, proves the accuracy of the above formula.

In the known combinations of the lactic acid with bases, only 1 atom of the water in the hydrated acid is replaced by 1 eq. of a metallic oxide; the acid in these salts is considered anhydrous. It appears, therefore, that the concrete acid, which is the hydrated acid *minus* 2 at. of water, is a product of the decomposition of the anhydrous acid, which has lost the elements of 1 at. water. This question can only be decided by new researches on the properties of the concrete acid, and by a minute study of all the lactates. Meantime it is very curious that, of the 2 atoms of water which the concrete acid takes up when boiled in solution, one only can be replaced by metallic oxides; that of zinc, for example.

Lactic acid dissolves a very large quantity of freshly precipitated phosphate of lime; a property which is not possessed by acetic acid, and which is doubtless of great importance in the animal economy. It coagulates albumen; it dissolves in cold milk without changing it, but coagulates it when the mixture is boiled.

LACTATES.

In the neutral lactates, the hydratic water of the acid is replaced by 1 eq. of metallic oxide. No acid lactates are known, but it appears that there exist basic lactates, which have not been studied. The general formula for the neutral lactates is $\bar{L},MO$. They are all soluble in water; but Braconnot employed the lactate of zinc, on account of its sparing solubility, to obtain a lactate free from foreign salts. The *Lactate of Oxide of Ethule* has not yet been obtained.

Lactate of Urea.—Formula, $\bar{L},C_2N_2H_4O_2$. (Cap and Henry.) Discovered in human urine by these chemists. This compound may be obtained directly by double decomposition from the lactate of lime and the oxalate of urea. The liquid, filtered from the oxalate of lime, is evaporated at a gentle heat and crystallized in vacuo near sulphuric acid.

To extract it from urine, the urine is evaporated to the consistence of syrup, the free acid is neutralized by chalk, and filtered to separate the salts which have been deposited on cooling. The filtered liquid is dried in the water-bath, and the residue digested in a gentle heat with a mixture of 2 parts alcohol and 1 part ether. The lactate of urea dissolves in this liquid, and is obtained by evaporation in yellowish prisms, which may be rendered colourless by charcoal, and by repeated crystallization.

The lactate of urea crystallizes in hexagonal prisms, which have a pungent and cooling taste, and attract moisture from the air. When moderately heated, it melts and volatilizes without change. When strongly heated it is decomposed, and leaves a carbonaceous residue. According to Cap and Henry, the lactate of urea is distinguished from the oxalate and nitrate of urea by this, that the latter contain 1 at. of combined water, which is not found in the former.

The *Lactates* of *Ammonia*, *Potash*, and *Soda*, are deliquescent, and do not crystallize.

The *Lactate of Baryta* is obtained by precipitating the lactate of zinc by baryta; it is very soluble in water, and when dry forms a semi-transparent amorphous mass. It is used in the preparation of lactic acid.

Lactate of Lime.—According to Corriol, the nux vomica contains this salt ready formed. It is obtained by making an aqueous infusion of nux vomica, evaporating to the consistence of syrup, and acting on the residue with boiling alcohol, which dissolves the lactate of lime. The alcohol is distilled off: after some time, the concentrated solution deposits the salt in the form of small granular crystals, which are purified by means of charcoal and recrystallization. Nux vomica contains 2 to 3 p. c. of lactate of lime.

This salt is easily obtained from sour whey, by evaporating it to the consistence of syrup, treating the residue with alcohol, and saturating the alcoholic solution with milk of lime or with chalk. The alcohol is then distilled off, and the residue dissolved in a little water and crystallized. (Henry.)

The lactate of lime crystallizes in colourless needles, grouped round a common centre: they are more soluble in hot than in cold water, and contain $29{\cdot}5 = 5$ at. water of crystallization, which is expelled when the salt is heated so that it melts.

Lactate of Zinc.—The best method of obtaining this salt is to exhaust sour-krout with boiling water, and to neutralize the decoction with carbonate of zinc. The filtered liquid is then evaporated to the consistence of syrup, and the crystals which form are decolorized by charcoal and by repeated crystallizations. The salt may also be obtained from sour whey by proceeding as directed for lactate of lime, substituting carbonate of zinc for chalk.

Lactate of zinc crystallizes by the cooling of a hot solution in four-sided prisms terminated by obliquely truncated summits: they contain 3 at. of water. Alcohol added to the watery solution causes the deposition of a basic salt, which is soluble and crystallizable; it appears to contain 3 at. oxide of zinc, but this requires confirmation.

The *Lactates of Alumina*, *Nickel*, *Lead*, and *Mercury*, are very soluble in water, and do not crystallize.

The *Lactate of Magnesia* crystallizes in small plates containing 3 at. water, and requires 30 parts of cold water to dissolve it.

The *Lactates of Protoxide of Iron*, $\bar{L},FeO$, 3 aq. *of Oxide of Copper*, $\bar{L},CuO$, 2 aq. *and of Silver*, are crystallizable.

METHULE.

Formula, C_2H_3. Symbol, Me.

The name of Methule has been given to the hypothetical radical of pyroxylic spirit and its combinations; it is analogous to ethule in its chemical characters, but differs essentially from it in composition.

The compounds of methule with oxygen, chlorine, bromine, and iodine, are formed by acting on the hydrate of oxide of methule with sulphuric acid, and the corresponding hydracids of chlorine, bromine, and iodine.

All the compounds of methule are obtained from the *pyroxylic spirit*, which was first discovered by Philip Taylor among the products of the dry distillation of wood.

It is to the important researches of Dumas and Peligot that we owe the knowledge of its composition, its chemical nature, and the various compounds which it forms. All the following details are taken from the memoir of these chemists. (Ann. de Chimie, vol. lviii. p. 5.)

OXIDE OF METHULE.

Formula, $C_2H_3O = MeO$. (Dumas and Peligot, Kane.) Syn. Hydrate of Methylene; Methylic Ether. It is prepared by distilling together equal volumes of oil of vitriol and pyroxylic spirit. The gases disengaged are made to pass first through milk of lime, and then through several bottles of pure water, which absorbs the oxide of methule. When this aqueous solution is gently heated, it gives off the oxide of methule, which may be collected over mercury. It is deprived of moisture and of pyroxylic spirit by the contact of caustic potash.

It is a colourless gas, having a very agreeable ethereal odour; it is very inflammable, and burns with a pale blue flame. It is not liquefied by a cold of 4°. It is dissolved by water, to which it gives an ethereal odour and a pungent taste. One volume of water absorbs 37 volumes of the gas. It is much more soluble in alcohol, also in pyroxylic spirit, and in oil of vitriol: the latter separates from it when water is added.

When this gas and the vapour of anhydrous sulphuric acid are mixed in a vessel carefully cooled, they unite to form the neutral sulphate of oxide of methule. (Regnault.)

By combining with oxygen acids, the oxide of methule forms neutral and acid salts. It contains the same elements as alcohol, united in the same proportions; but its molecule is only half as large, and the density of its vapour is 1·605, which represents 2 volumes, while that of alcohol represents 4 volumes. The calculated density of oxide of methule is $\frac{3{\cdot}1403}{2} = 1{\cdot}570$.

HYDRATE OF OXIDE OF METHULE.

Formula, $C_2H_3O,aq. = MeO,aq.$

Syn. Pyroxylic Spirit; Bihydrate of Methylene.

The pyroxylic spirit of commerce is very impure; it contains, besides the hydrate of oxide of methule, which forms the chief part of it, acetone and other inflammable liquids.

To purify it, we avail ourselves of the property which it has of forming a compound with chloride of calcium, which is with difficulty decomposed by a heat of 212°. The raw spirit is introduced into a retort with an excess of chloride of calcium, and the mixture is distilled in the water-bath as long as volatile matter passes off.

A quantity of water equal to the spirit employed is then added, and the distillation is continued. The product is now pure pyroxylic spirit, carrying along with it a little water, which is removed by a second distillation with quicklime. It sometimes happens that the first drops of hydrate of oxide of methule which pass become turbid on the addition of water. In this case, the receiver must be changed.

Pure pyroxylic spirit is a very mobile, colourless liquid, having a peculiar empyreumatic odour, resembling at the same time that of alcohol and that of acetic ether. It is very inflammable, and burns with a pale flame. It mixes perfectly with water, also with alcohol and ether, and is neutral to test paper. It boils at about 150°; its sp. g. at 68° is 0·798. The density of its vapour is 1·120, representing 4 volumes. Calculation gives $\frac{4{\cdot}4411}{4} = 1{\cdot}11$.

When the hydrate of oxide of methule is distilled with hyperoxide of manganese and sulphuric acid, or when its vapour is brought into contact with the powder of platinum and the air, a series of oxidized products is obtained, among which are observed *formic acid* and *formomethylal.*

An excess of nitric acid, with the aid of heat, converts the pyroxylic spirit into water and oxalic acid. By adding nitrate of silver to the mixture, and evaporating so as to expel the nitric acid, we obtain a white residue of oxalate of silver. Chlorine decomposes pyroxylic spirit with facility, giving rise to a variety of products containing chlorine.

In contact with potassium, pyroxylic spirit disengages pure hydrogen; there is formed a compound of potash with oxide of methule, which remains in solution. (Böckmann.) The statements of Löwig concerning this reaction (Repert. de Chimie, vol. iv.) are inexact.

The hydrate of oxide of methule dissolves small quantities of sulphur and phosphorus with the aid of heat; it also dissolves many resins. It mixes with most essential oils; and forms crystalline compounds with baryta, lime, and chloride of calcium.

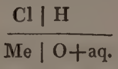
Hydrate of Oxide of Methule and Baryta.—Formula, $MeO,aq. + BaO$. (Dumas.) Pure baryta dissolves easily in pyroxylic spirit, with the evolution of much heat; the solution becomes brown when exposed to the air. Evaporated in vacuo, it deposits silky needles, fusible when heated. When calcined, they leave a residue of carbonate of baryta and carbon. When the heat is first applied, pyroxylic spirit is given off; afterwards an oily liquid passes over.

According to Dumas and Peligot, the crystals contain 70·5 p. c. of baryta, whence they deduce the above formula.

Hydrate of Oxide of Methule and Chloride of Calcium.—Formula, $2(MeO,aq.)+CaCl$. (Kane.) The hydrate of oxide of methule dissolves chloride of calcium with great facility, becoming hot when the solution is concentrated; it forms, on cooling, a crystalline mass; if less concentrated, it forms large six-sided tables, deliquescent in a moist atmosphere. When dried in vacuo over sulphuric acid, they leave, when calcined, a residue of 46·7 p. c. of chloride of calcium. Water decomposes this compound, separating the pyroxylic spirit.

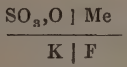
COMPOUNDS OF METHULE WITH THE NEGATIVE NON-METALLIC BODIES, AND WITH SULPHUR.

The compounds of methule with chlorine, bromine, and iodine, may be obtained, either directly by the action of a hydracid on the hydrate of oxide of methule, or by distilling the sulphate of oxide of methule with the corresponding haloid salt. In the former case, the oxygen of the oxide of methule combines with the hydrogen of the hydracid, forming water, while the negative element of the hydracid takes its place. Thus, for example, hydrochloric acid, acting on hydrate of oxide of methule, gives chloride of methule and 2 eq. of water,



$$\frac{Cl \mid H}{Me \mid O+aq.}$$

In the latter case, the metal of the haloid salt is oxidized at the expense of the oxide of methule, forming a metallic oxide, which in its turn combines with sulphuric acid, while the negative element of the salt combines with the methule which is set free. Thus, when sulphate of oxide of methule acts on fluoride of potassium, there are formed sulphate of potash and fluoride of methule.



$$\frac{SO_3,O \mid Me}{K \mid F}$$

The compounds of methule with chlorine, bromine, &c. are neutral to test paper. Water does not affect them, and an aqueous solution of a caustic alkali decomposes them with much difficulty. On the other hand, a solution of caustic alkali in alcohol, or pyroxylic spirit, readily converts them into haloid salts and hydrate of oxide of methule. Metallic solutions cannot detect the chlorine, bromine, &c. in the solutions of these compounds in alcohol or pyroxylic spirit.

These compounds are very inflammable; the hydracid of their negative element is a constant product of their combustion. Thus chloride of methule, in burning, gives off hydrochloric acid. When they are passed through a red-hot tube, they are resolved into the hydracid, gaseous carbo-hydrogens, and a residue of carbon.

Chloride of Methule.—Formula, $C_2H_3 + Cl = MeCl$. (Dumas and Peligot.) Syn. Hydrochlorate of Methylene. This compound is best obtained by distilling sulphate of oxide of methule with chloride of sodium; or by heating a mixture of common salt, sulphuric acid, and pyroxylic spirit. The product is collected under water, which retains sulphurous acid, pyroxylic spirit, and oxide of methule, if any should accidentally be disengaged. The chloride of methule is a colourless gas, having an ethereal odour and a sweet taste. Water at 60° dissolves 2·8 times its volume under the ordinary pressure. It burns with a white flame edged with green. Its sp. g. is 1·7378, representing 4 volumes. The calculated density is $\frac{6\cdot9189}{4} = 1\cdot729$. It is not liquefied by a cold of 0°.

According to Regnault, chlorine, aided by the direct rays of the sun, decomposes this substance, forming hydrochloric acid, and several new compounds containing chlorine. (See below, "Combinations of Formule with Chlorine," and "Action of Chlorine, &c. on Methule.")

Iodide of Methule.—Formula, MeI. (Dumas and Peligot.) It is prepared by distilling a mixture of 12 to 15 parts of pyroxylic spirit, 8 parts of iodine, and 1 part of phosphorus; the latter added by degrees in fragments. By adding water to the product, the iodide is at once separated; it is purified by redistillations along with chloride of calcium and oxide of lead. It is a colourless liquid, burning with difficulty. It boils between 104° and 122°: its density at 70° is 2·237.

Fluoride of Methule.—Formula, MeF. (Dumas and Peligot.) Obtained by distilling sulphate of oxide of methule with fluoride of potassium. It is a colourless gas, having a pleasant ethereal odour: its density is 1·186. It is inflammable, and burns with a blue flame. Water absorbs 1·5 time its volume.

Cyanide of Methule.—Obtained by distilling sulphate of oxide of methule with cyanide of potassium. An ethereal liquid, insoluble in water. (Dumas and Péligot.)

Sulphuret of Methule.—Formula, $C_2H_3S = MeS$. (Regnault.) It is easily obtained by the action of chloride of methule on an alcoholic solution of protosulphuret of potassium. The latter is placed in a tubulated retort furnished with an adopter and a receiver. A current of chloride of methule is introduced by the tubulure; and, when the solution is saturated with it, a gentle heat is applied to the retort, while the current of chloride of methule is continued. A volatile liquid condenses in the receiver, which must be carefully cooled. It is washed several times with water, and rectified with chloride of calcium. When an alkaline sulphuret is distilled with the sulphate of oxide of methule, there is also obtained an ethereal liquid of a disagreeable alliaceous smell, which appears to be nothing else than sulphuret of methule. (Dumas and Peligot.) The sulphuret of methule is a very mobile liquid, having a very offensive smell. Its density is 0·845 at 70°; it boils at 106°. The density of its vapour has been found to be 2·115, representing 2 volumes. The calculated density is $\frac{4.3164}{2} = 2{\cdot}158$. (Regnault.) Chlorine acts energetically on this compound, producing several new substances. (See below, "Products of the Decomposition of Methule, and the Substances derived from it.")

Hydrosulphuret of Sulphuret of Methule.—When heat is applied to a mixture of the double sulphate of potash and oxide of methule with the hydrosulphuret of sulphuret of potassium, an extremely volatile liquid is obtained, having an alliaceous odour very similar to that of the corresponding compound of ethule (mercaptan). It is a colourless liquid, lighter than water; it boils at 70°, and acts like mercaptan on the oxides of lead and mercury. The compound with mercury crystallizes from alcohol in brilliant white scales, which do not melt at 212°. (W. Gregory.)

OXYGEN SALTS OF METHULE.

The oxide of methule, by combining with the oxygen acids, produces neutral and acid salts. In the neutral salts, the hydratic water of the acid is replaced by 1 eq. of oxide of methule. The acid salts contain 1 eq. of neutral salt and 1 eq. of the hydrated acid.

These salts exhibit, with the metallic salts, the same reactions as the salts of oxide of ethule; thus, knowing the history of the latter, it is easy to deduce that of the compounds of oxide of methule.

The anhydrous metallic oxides have no action on them; while the hydrated alkalies decompose them with great facility. Löwig had stated that in this case no hydrate of oxide of methule is formed; but the experiments of Malaguti and Böckmann have proved that this assertion is altogether erroneous.

Neutral Sulphate of Oxide of Methule.—Formula, MeO,SO_3. (Dumas and Peligot.) Syn. Sulphate of Methylene. When concentrated sulphuric acid is mixed with pyroxylic spirit, a reaction takes place similar to that between the same acid and alcohol; that is to say, there is formed bisulphate of oxide of methule, which, when heated, is resolved into sulphurous acid, carbon, oxide of methule, and neutral sulphate of oxide of methule. The quantity of the latter increases as we increase the proportion of sulphuric acid. All the other phenomena in this reaction are the same as in the action of sulphuric acid on alcohol. It has been already mentioned that the gaseous oxide of methule combines directly with anhydrous sulphuric acid to produce the neutral sulphate.

To obtain this compound, 1 part of pyroxylic spirit is distilled with 8 or 10 parts of oil of vitriol. The neutral sulphate collects in the receiver as an oily liquid. It is washed with cold water to remove the acid, dried by means of chloride of calcium, and rectified with quicklime to remove sulphurous acid.

It is a colourless liquid, having an alliaceous smell. Its sp. g. is 1·324 at 70°. It boils at 370°, and distils unchanged. The density of its vapour is 4·3634; hence it is composed of equal volumes of anhydrous sulphuric acid, and of oxide of methule condensed into 1 volume.

It is slowly decomposed by cold water, forming bisulphate of oxide of methule and hydrate of oxide of methule. It is not changed by being heated with anhydrous alkalies, or metallic oxides; but the hydrated alkalies quickly decompose it, forming hydrate of oxide of methule, and a double sulphate of the alkali with oxide of methule.

Heated with a metallic chloride, cyanide, &c. or with an alkaline benzoate, succinate, &c. it yields chloride or cyanide, &c. of methule, or benzoate, succinate, &c. of oxide of methule; and these products, being volatile, pass into the receiver.

By ammonia, dry or dissolved, it is acted on, producing *Sulphamethylan.*

The neutral sulphate may be employed to yield all the other compounds of oxide of methule.

Bisulphate of Oxide of Methule.—Formula, $MeO,aq.,2SO_3$. Syn. Sulphomethylic Acid. This compound is formed when sulphuric acid is mixed with pyroxylic spirit, or when the neutral sulphate is boiled with water. It was discovered at the same time by Dumas and Peligot, and by Kane. It is easily obtained by cautiously adding diluted sulphuric acid to a solution of the double sulphate of baryta and oxide of methule. The filtered liquid is evaporated in vacuo over sulphuric acid. It may also be prepared by decomposing the double sulphate of lead and oxide of methule by sulphuretted hydrogen. The solution of the neutral sulphate of oxide of methule in boiling water, if allowed to evaporate spontaneously, yields this compound very pure.

It is a colourless, syrupy liquid, very acid; which, in a dry atmosphere, forms a mass composed of white needles. When prepared from the salt of baryta, it is decomposed in vacuo, giving off sulphurous acid; it is more stable when made from the neutral sulphate. Heat accelerates its decomposition.

It mixes in all proportions with water, and is soluble in alcohol. In contact with bases, it forms double salts, in which the hydratic water of the acid is replaced by 1 eq. of metallic oxide. All these salts are soluble in water.

DOUBLE SALTS OF THE SULPHATE OF OXIDE OF METHULE.

Syn. Sulphomethylates. These double salts, when their solutions are boiled or evaporated, undergo decomposition, yielding products exactly analogous to those formed from the corresponding salts of ethule.

When subjected to dry distillation, they yield, among other products, a large quantity of neutral sulphate of oxide of methule.

The double salts of sulphate of oxide of methule with *ammonia* and *oxide of ethule* have not yet been formed.

Sulphate of Potash and Oxide of Methule.—Formula, $MeO,KO,2SO_3+aq.$ (Kane.) This salt is obtained by precipitating the double salt of baryta by carbonate of potash. It crystallizes in rhomboidal tables, which have the lustre of mother-of-pearl, and are deliquescent in a moist air. They differ from the corresponding salt of ethule in containing water of crystallization.

When this salt is dissolved in a strong solution of ferrocyanide of potassium, there are obtained, by the evaporation of the mixture, two salts: first, a yellow salt, easily crystallizable, insoluble in alcohol, very similar in aspect to the ferrocyanide of potassium; and afterwards a white salt, which is soluble in alcohol. These salts were discovered by Gregory. They are double salts: the yellow salt is a compound of ferrocyanide of potassium with ferrocyanide of methule; the white appears to contain cyanide of methule, bisulphate and sulphate of potash, and oxide of methule. Similar compounds are obtained by treating in the same way the corresponding salt of ethule. (Gregory.) These compounds merit a more minute investigation.

Sulphate of Baryta and Oxide of Methule.—Formula, $MeO, BaO, 2SO_3 + 2aq.$ (Dumas and Peligot.) To obtain it, equal weights of oil of vitriol and pyroxylic spirit are mixed, and heated to the boiling point. When cold, water is added, and the liquid is neutralized, first with carbonate of baryta, and finally with pure baryta. After removing the excess of baryta by a current of carbonic acid, the filtered liquid is gently evaporated. The double salt crystallizes in square tables, colourless and transparent, efflorescing in the air. In vacuo, they lose all their water of crystallization and become opaque. This salt is used for the preparation of the bisulphate of oxide of methule; and, when mixed with soluble sulphates, it yields the other double salts of methule.

Sulphate of Lead and Oxide of Methule.—Formula, $MeO, PbO, 2SO_3 + aq.$ (Kane.) Prepared in the same way as the preceding salt. It is deliquescent. Kane has sometimes obtained it in the same form as the salt of baryta, and containing 2 at. of water of crystallization.

The *Phosphate of Oxide of Methule* has not yet been obtained.

Nitrate of Oxide of Methule.—Formula, MeO, NO_5. (Dumas and Peligot.) The action of nitric acid on pyroxylic spirit is different from its action on alcohol. The latter is easily decomposed by it, yielding oxidized products, with nitrate of oxide of ethule: the latter is only changed by it when boiled. A large excess of nitric acid converts it into formic and oxalic acids, without any nitrite or nitrate of oxide of methule. The nitrite appears not to exist: the nitrate, on the contrary, is easily obtained.

For this purpose, 1 part of nitre is introduced into a retort with a mixture of 2 parts of oil of vitriol and 1 part of pyroxylic spirit. The mass becomes very hot, and the new compound distils over without external heat. The receiver must be carefully cooled; and in it two liquids condense, of which the heavier is nitrate of oxide of methule. It is mixed with a very volatile compound, perhaps formiate of oxide of methule, and has the odour of prussic acid. To purify it, it is rectified with an excess of chloride of calcium and oxide of lead. The last portions are perfectly pure.

It is a colourless liquid, having a faint ethereal smell. Its density is 1·182 at 72°; it boils at 151°; is inflammable, and burns with a yellow flame. Its vapour, heated above 248°, detonates with great violence; producing water, carbonic acid, and deutoxide of nitrogen. It is soluble in water, and miscible in all proportions with alcohol, ether, and pyroxylic spirit.

It is slowly decomposed by aqua ammoniæ or aqua potassæ; rapidly by an alcoholic solution of potash. The products are nitrate of potash and pyroxylic spirit.

Carbonate of Oxide of Methule.—The neutral salt is not known. The double salts which it forms with the alkaline carbonates are obtained in the same way as the corresponding salts of ethule.

Oxalate of Oxide of Methule.—Formula, $MeO,\bar{O}$. (Dumas and Peligot.) To obtain it, equal parts of sulphuric acid, oxalic acid, and pyroxylic spirit are distilled; or 2 parts of sulphuric acid may be distilled with one part of binoxalate of potash and 1 part of pyroxylic spirit. The oxalate is obtained in the receiver, partly pure, in the form of crystals, partly dissolved in pyroxylic spirit. The whole is allowed to evaporate in a warm place; the crystals are dried by pressure in bibulous paper, and redistilled with oxide of lead to remove any free oxalic acid.

This compound forms a white, solid, transparent mass, composed of rhomboidal tables. It melts at 124°, and boils at about 322°. It is easily dissolved by water, producing hydrated oxalic acid and pyroxylic spirit. It is soluble in alcohol and pyroxylic spirit, more so with the aid of heat; and these solutions, saturated when hot, deposit large transparent crystals on cooling.

Dry ammonia converts it into oxamethylane; aqua ammoniæ converts it into oxamide and pyroxylic spirit. The reaction is the same as with the corresponding compound of ethule.

The *Binoxalate of Oxide of Methule* is not known.

Oxalate of Oxide of Methule and Oxamide.—Formula, $C_6H_5NO_6 = MeO,\bar{O} + C_2O_2,Ad$. (Dumas and Peligot.) Syn. Oxamethylane. When a current of dry ammonia is passed over melted oxalate of methule, the latter is gradually converted into a white solid mass. Alcohol dissolves it, and by evaporation deposits the oxamethylane in cubical crystals with the lustre of mother-of-pearl.

Bisulphocarbonate of Oxide of Methule.—Formula, $2CS_2,MeO$. This compound is formed in the same way as the corresponding compound of ethule. According to Dumas and Peligot, the double sulphocarbonate of oxide of methule and potash may be obtained by adding hydrate of potash to a solution of the bisulphuret of carbon in pyroxylic spirit.

Bicyanurate of Oxide of Methule.—Formula, $2Cy_3O_3,3MeO$, 6 aq. (Richardson.) The preparation, properties, and reactions of this compound are entirely analogous to those of the corresponding compound of ethule formerly described.

Benzoate of Oxide of Methule.—Formula, $BzO,MeO = C_{14}H_5O_3, C_2H_3O$. (Dumas and Peligot.) This compound is best obtained by distilling a mixture of dry benzoate of lime or of soda with neutral sulphate of methule, or 2 parts of benzoic acid with 1 part of sulphuric acid and 1 part of pyroxylic spirit. It is an oily colourless liquid, having a balsamic odour, not unlike that of the oil of bitter almonds. It is heavier than water, and boils at 227°: insoluble in water; soluble in alcohol, pyroxylic spirit, and ether. The density of its vapour is found to be 4·7506, representing 4 volumes; the calculated density is $\frac{18\cdot996}{4} = 4\cdot749$.

Acetate of Oxide of Methule.—Formula, $MeO,AcO_3 = C_2H_3O, C_4H_3O_3$. (Dumas and Peligot.) This compound is prepared by distilling 2 parts of pyroxylic spirit with 1 of hydrated acetic acid and 1 of oil of vitriol. An acetate may be substituted for the acetic acid. The product is put in contact with fragments of chloride of calcium, which, combining with the free pyroxylic spirit, separates the acetate as a light liquid. According to Berzelius, it is contained in abundance in the raw pyroxylic spirit. Reichenbach, having extracted it therefrom, although not in a state of purity, considered it as a peculiar combination, to which he gave the name of Mesite. Berzelius has given a process by which it may be extracted from the raw liquor. The presence of a large proportion of this substance is the cause of the fluidity of wood-tar.

It is a colourless liquid, having a pleasant smell, like that of pyroxylic spirit, and a burning taste. Its sp. g. is 0·919 at 70°. It boils at 136°. (Dumas and Peligot.) The mesite of Reichenbach has the sp. g. 0·805, and boils at 144°. The acetate of methule dissolves $\frac{1}{2}$ part of water, and is itself dissolved by 2 parts of water. It mixes in all proportions with alcohol and pyroxylic spirit, and is separated from these solutions by chloride of calcium and hydrate of potash. Chlorine decomposes it, producing hydrochloric acid. When mixed with oil of vitriol, it becomes very hot, and is decomposed. Hydrate of lime converts it into acetate of lime and pyroxylic spirit.

It dissolves many salts, vegetable acids, oils both fixed and volatile, and several resins. It contains the same elements, in the same proportions but differently grouped, as the formiate of oxide of ethule; for $C_2H_3O,C_4H_3O_3 = C_4H_5O,C_2HO_3 = C_6H_6O_4$.

Mucate of Oxide of Methule.—Formula, $2MeO + \overline{Mu}$. (Malaguti.) Prepared exactly as the mucate of ethule, using pyroxylic spirit instead of alcohol. It is a white crystalline substance, decomposed by a heat of 326°. It is soluble in alcohol, from which it crystallizes in six-sided rhombic prisms. It is very soluble in water. The crystals from its aqueous solution have a density of 1·53; whereas those formed in alcohol have a density only of 1·48.

COMPOUNDS OF METHULE OF UNCERTAIN CONSTITUTION.

Oxychlorocarbonate of Oxide of Methule.—Formula, $C_4H_3ClO_4$. (Dumas and Peligot.) The preparation and properties of this body are similar to those of the corresponding compound of ethule. Dumas and Peligot express its constitution by the formula $C_2\left.\begin{matrix}O_3\\Cl\end{matrix}\right\} + C_2H_3O$. According to this, it would be composed of oxide of methule united to a peculiar acid.

Urethylane.—The preceding compound, in contact with ammonia, appears to undergo a change analogous to that described under the corresponding compound of ethule. Dumas and Peligot have shown that there are formed sal-ammoniac and a deliquescent crystallizable mass, to which they have given the name of Urethylane, corresponding to urethane, formerly described.

Sulphamethylane.—When a current of dry ammonia is passed through neutral sulphate of methule, heat is developed, and a new substance is formed, to which Dumas and Peligot have given the name of Sulphamethylane. It may also be obtained by using aqua ammoniæ. In this case a liquid is obtained, which, if evaporated in vacuo, deposits large crystals of the new compound. It is very deliquescent. Its empirical formula is $C_2H_5NS_2O_6$. It is a compound analogous to oxamethylane: if the latter be represented by

$$C_2O_3,C_2H_3O+C_2O_2,Ad,$$

sulphamethylane will be represented by

$$SO_3,C_2H_3O+SO_2,Ad;$$

that is, a compound of sulphate of methule with sulphamide.

PRODUCTS OF THE DECOMPOSITION OF METHULE AND OF THE SUBSTANCES DERIVED FROM IT.

Hitherto we have but few exact researches on the transformations of methule and its compounds. With reference to the existence of an acid corresponding to isethionic acid, Dumas and Peligot have found, that, when anhydrous sulphuric acid is mixed with pyroxylic spirit, the mixture being carefully cooled, an acid is obtained, which forms with baryta a soluble and crystallizable salt, having the same composition as the double sulphate of methule and baryta, but differing from that salt in its properties.

When pyroxylic spirit is oxidized by means of the powder of platinum and air, as described under alcohol, it undergoes a slow combustion, similar to that of alcohol in the same circumstances. The oxygen of the air, condensed by the platinum, combines with the hydrogen of the spirit, and replaces that which is removed, equivalent for equivalent. The final product of this reaction is a very acid liquid, which is found to be pure formic acid.

1 eq. hydrate of oxide of methule . .	$C_2H_3O+aq.$
loses 2 eq. of hydrogen	H_2
The residue	$C_2HO+aq.$
combines with 2 eq. of oxygen .	O_2
and yields hydrated formic acid . .	$C_2HO_3+aq.$

It is obvious that there is the same relation between pyroxylic spirit and formic acid, as between alcohol and acetic acid. We have, therefore, good reason to believe that formic acid is the oxide of a radical, C_2H, analogous to acetule, which has been called *Formule.* By formule, then, is to be understood a hypothetical radical whose formula is C_2H.

We shall describe the changes produced on methule and its compounds by chlorine, &c. in treating of the compounds of formule with chlorine, bromine, &c.

FORMULE.

Formula, C_2H. Symbol, Fo. As ethule may be considered as the hyduret of acetule, AcH_2; so methule may be viewed as the hyduret of formule, FoH_2. We shall then have

FoH_2 = methule.
FoH_2O = oxide of methule.
$FoH_2O+aq.$ = hydrate of oxide of methule.
$FoO_3 +aq.$ = hydrated formic acid.

The compound corresponding to aldehyde has not yet been discovered. Its formula would be $FoO + aq. = C_2HO + aq.$ In like manner, the compound analogous to the aldehydic or acetulous acid is not yet known. The following table contains the principal compounds of the series of formule:—

C_2HO	oxide of formule, unknown.
$C_2HO +aq.$	hydrate of the above, contained in formomethylal.
C_2HO_3	anhydrous formic acid.
$C_2HO_3+aq.$	hydrated formic acid.
C_2HCl_3	perchloride of formule.
C_2HBr_3	perbromide of formule.
C_2HI_3	periodide of formule.

Gregory first observed that by distilling a mixture of pyroxylic spirit, hyperoxide of manganese, and sulphuric acid, a peculiar liquid is obtained. Kane subsequently examined this substance with care, and described it under the name of *Formomethylal.* He prepared it by distilling 2 parts of pyroxylic spirit with 3 parts of oil of vitriol, previously mixed with 3 parts of water and 2 parts of hyperoxide of manganese. The reaction is very violent; so that it is necessary to employ a water-heat, and to cool the receiver carefully. The product is very impure, containing several liquids. It begins to boil at 100°, but the boiling point gradually rises to 177°. The liquid which passes first reduces the nitrate of silver with the aid of ammonia and a gentle heat, as aldehyde does. A liquid then comes, which boils steadily at 100°. This is Kane's formomethylal. Several analyses led to the formula $C_4H_5O_3$; according to which, it might be either a compound of

1 at. oxide of methule . . .	C_2H_3O
and 1 at. hydrate of oxide of formule .	$C_2H\ O+HO$
	$C_4H_4O_2+HO$,

or a compound of

1 at. formic acid . . .	$C_2H\ O_3$
and 3 at. oxide of methule . . .	$C_6H_9\ O_3$
	$C_8H_{10}O_6=2(C_4H_5O_3)$.

In support of the latter view,—namely, that it is a tribasic formiate of methule,—Kane adduced the fact, that, when treated with an alcoholic solution of potash, it yields formiate of potash and pyroxylic spirit. But Malaguti showed that the quantity of formic acid produced was never more than half of that indicated by the formula ; and in the course of his researches he succeeded in proving that it is a mixture of neutral formiate of methule and another liquid, which he has named *Methylal.*

Methylal.—Formula, $C_6H_8O_4$. (Malaguti.) To obtain it, the product of the distillation above described is mixed with water, and distilled with potash ley. The product is saturated with solid caustic potash, which separates an ethereal liquid. This is mixed with water and again rectified with potash, so as to purify it entirely from formiate of oxide of methule.

Methylal is an ethereal liquid of an agreeable odour. It is dissolved by three parts of water, from which it is separated by caustic potash or chloride of calcium. It is miscible in all proportions with pyroxylic spirit, alcohol, and ether. It boils at 108°, and has the sp. g. 0·855. It is inflammable, and burns with a luminous flame. Oxidizing agents convert it into formic acid. Chlorine destroys it ; producing, among other products, sesquichloride of carbon. (Malaguti.) According to the formula, $C_6H_8O_4$, representing 4 vol. of vapour, this substance may be regarded as a compound of 1 at. oxide of formule, and 2 at. hydrate of oxide of methule $= C_2HO, HO + 2C_2H_3O$.

Regnault has started a very ingenious conjecture relative to the formation of this compound. He supposes that 3 at. of oxide of methule, formed by the action of the sulphuric acid on the pyroxylic spirit, group themselves into one $= C_6H_9O_3$; this, again, exposed to the oxidizing agency of the hyperoxide of manganese, loses 1 at. hydrogen, which is replaced by 1 at. oxygen, thus yielding the compound $C_6H_8O_4$.

The corresponding compound in the series of ethule is acetal, $C_8H_9O_3$, which we have considered as a compound of 1 at. hydrated oxide of acetule (aldehyde), and 1 at. oxide of ethule $=$ AcO,HO + AeO. Regnault explains its formation in a manner analogous to that proposed by him for methylal, supposing 2 at. of oxide of ethule to be grouped into one $= C_8H_{10}O_2$; and that this losing 1 at. of hydrogen, and gaining 1 at. oxygen, yields acetal. These different views are essentially the same.

FORMIC ACID.

Formula, C_2HO_3+aq. The production of this acid by the oxidation of the hydrated oxide of methule (pyroxylic spirit), has been already described. It was first discovered in the red ant (formica rufa), whence its name; Gehlen first recognized it as a peculiar acid. Doebereiner was the first who prepared it artificially by distilling tartaric acid with sulphuric acid and hyperoxide of manganese. All vegetable substances produce formic acid, carbonic acid, and sometimes acetic acid, when distilled with nitric acid, periodic acid, iodic acid, hypermanganic acid, a mixture of chromic and sulphuric acids, or of sulphuric acid with hyperoxide of manganese.

Formic acid is further produced by the action of alkalies on chloral, and by the decomposition of metallic cyanides or hydrocyanic acid by strong acids or alkalies. It is likewise a product of the dry distillation of effloresced (monohydrated) oxalic acid, and of the distillation of organic matters with fused potash at a high temperature.

To obtain the hydrated formic acid, C_2HO_3+aq. dry formiate of lead in fine powder is introduced into a long glass tube; one end of which is connected with a receiver, the other with an apparatus from which sulphuretted hydrogen gas is disengaged. When the formiate of lead is entirely decomposed, which is known by its becoming black throughout, the formic acid is driven into the receiver by a very gentle heat. If the heat be too strong, decompositions of a different kind occur, producing sulphuretted compounds not yet examined. To purify the acid obtained from any excess of sulphuretted hydrogen, it is boiled for a very short time.

The hydrated formic acid is a limpid and colourless liquid, which fumes slightly, and attracts the moisture of the air. It has a penetrating odour, and below 32° it crystallizes in brilliant scales. It boils at 212°, and has the sp. g. 1·2353. The vapour of the boiling acid is inflammable, and burns with a blue flame.

It is miscible with water in all proportions. With a quantity of water equal to that which it already contains (20 p. c.), it forms a second hydrate, C_2HO_3+2 aq. which has the same properties as the first, except that it boils at 223°, and does not solidify at 5°, and that its sp. g. is 1·1104 at 60°. This second hydrate is easily obtained by distilling, in a bath of chloride of calcium, 18 parts of dry formiate of lead, 6 of oil of vitriol, and 1 of water.

Both these hydrates are exceedingly corrosive; a drop of either placed on a tender part of the skin produces an actual burn, which suppurates, causing intolerable pain, and is very difficult to heal. A more diluted acid, but equally pure, is obtained by distilling 10 parts of formiate of lime, 8 parts of oil of vitriol, and 4 of water. These proportions yield 9 parts of formic acid, sp. g. 1·075.

In order to obtain a diluted and impure acid, from which the salts of formic acid may be obtained, bruised ants may be distilled with water; or, according to Emmet, equal volumes of sulphuric acid, water, and wheat, rye, or starch, may be heated till the mixture blackens. It is then allowed to cool; and, after adding water equal to one-third of the whole bulk of the mixture, distilled in a copper alembic. The acid liquor obtained is turbid from the presence of oily matter, and contains much sulphurous acid. Phosphoric acid or chloride of tin may be substituted for the sulphuric acid in this operation, which proves that the oxygen of the sulphuric acid is not concerned in the production of the formic acid; but the reaction by which it is formed is not understood.

By distilling 1 part of starch with 4 of hyperoxide of manganese in fine powder, 4 of oil of vitriol, and 4 of water, we may obtain an impure formic acid, sp. g. 1·025: 100 parts of such acid neutralize 10·6 parts of dry carbonate of soda. When the mixture is heated there is a great disengagement of carbonic acid, so that it froths up very much. Hence it is better to introduce into the alembic first the oxide of manganese, the starch, and the water; to heat the mixture to 104°, and then to add the acid by degrees. When all the acid has been added, and the frothing is over, heat is applied, and 4½ parts of liquid are distilled off.

The best proportions for preparing formic acid on a smaller scale in glass vessels are 10 parts of starch, 37 of oxide of manganese, 30 of oil of vitriol, and 30 of water. The retort ought to have a capacity equal to 10 times the bulk of the mixture. These materials yield 3·35 parts of an acid, of which 100 parts neutralize 15 of dry carbonate of soda.

Formic acid is easily recognized by the reactions which it exhibits with sulphuric acid, and with the oxides of mercury and silver. An excess of sulphuric acid decomposes it without blackening, with a brisk effervescence; producing carbonic oxide gas, and water, which combines with the sulphuric acid.

When formic acid is heated with the oxide of mercury or of silver, it is completely destroyed; carbonic acid gas is disengaged, water is produced, and the metal is reduced, no trace of it remaining in the liquid. If the formic acid contain acetic acid, the latter is found in the liquid, in combination with the oxide of mercury or of silver.

Corrosive sublimate, heated with formic acid, is reduced to calomel, while hydrochloric and carbonic acids are disengaged.

The soluble salts of mercury and silver are reduced by formic acid just as the oxides are.

Peroxides are reduced, when heated with formic acid, to protoxides, which combine with the formic acid, carbonic acid being disengaged.

FORMIATES.

Formic acid has a stronger affinity for bases than acetic acid. Its salts may be obtained by saturating the acid with an oxide or a carbonate. They are all soluble in water. The alkaline formiates, when heated, blacken; give off inflammable gases, and leave a residue of carbonate. The other formiates, in the same circumstances, give off carbonic acid, carburets of hydrogen, and water; and leave a residue of carbon, and of oxide or reduced metal.

When a formiate in excess is boiled with the solutions of mercury, silver, platinum, and gold, the metals are completely reduced, with disengagement of carbonic acid gas. Sulphuric acid acts on the formiates as it does on the free acid. The salts of sesquioxide of iron are coloured of a deep yellowish red by the formiates.

Formiate of Ammonia.—Formula, $FoO_3,NH_3,HO = FoO_3,AdH_2O$. The solution of this salt becomes acid when evaporated, ammonia being disengaged. It crystallizes in four-sided rectangular prisms, terminated by four faces. It is deliquescent, has a cool and pungent taste, melts at 248°, and is volatilized without residue at a higher temperature. It contains the elements of 1 eq. hydrocyanic acid and 4 eq. water.

$$C_2HO_3,NH_4O = C_2NH,4HO.$$

It is actually transformed into these products when its vapour is passed through a red-hot tube. (Doebereiner; Pelouze.)

Formiate of Melamine.—This salt crystallizes in shining scales, which lose a part of their acid when exposed to the air, especially if heated to 212°.

Formiate of Oxide of Ethule.—Formula, FoO_3,AeO. Syn. Formic Ether. To prepare it, 7 parts of dry formiate of soda are introduced into a retort connected with a refrigeratory, along with a mixture of 10 parts of oil of vitriol, and 6 of alcohol at 90 p. c. By the heat spontaneously developed, the greater part of the formic ether distils without the application of external heat. It is purified from acid by agitation with milk of lime, and from water by chloride of calcium, which is added as long as it is moistened.

The formiate of ethule is a limpid liquid, of a penetrating aromatic smell, and has the sp. g. 0·912. It boils at 128°; its taste is cooling and spicy. It is soluble in 10 parts of water, and miscible in all proportions with alcohol, ether, pyroxylic spirit, and several fixed and volatile oils. It quickly becomes acid when exposed to the air.

Formiate of Oxide of Methule.—Formula, FoO_3,MeO. Prepared like the preceding compound. A very mobile liquid, lighter than water; boiling about 98°. Its odour resembles that of acetic ether.

Formiate of Potash.—A deliquescent salt, which can hardly be crystallized.

Formiate of Soda.—Formula, $FoO_3,NaO + 2\,aq$. Prepared by decomposing formiate of lead with carbonate of soda. It crystallizes in rhombic prisms or tables, of a bitter saline taste. When heated, they melt in their water of crystallization; and at a higher temperature they are decomposed. It is deliquescent in a moist air; insoluble in alcohol. According to Goebel, this salt, when heated with a great many metallic oxides, in the dry state, reduces them. He recommends it as a powerful reducing flux for blowpipe experiments. Doebereiner has proposed to employ its solution to separate silver, mercury, platinum, and palladium from iron, copper, manganese, &c. When solutions containing these metals are boiled with formiate of soda, the former are precipitated in the metallic state; the latter are not affected.

Formiate of Baryta.—Formula, FoO_3,BaO. This salt crystallizes easily in transparent prisms of a high lustre, permanent in the air. It is very bitter to the taste, soluble in 4 parts of water, insoluble in alcohol. (Arfvedson.)

Formiate of Strontia.—Formula, $FoO_3,SrO + 4\,aq$. Six-sided prisms, brilliant and transparent, permanent in the air. Heat expels the water of crystallization.

Formiate of Lime.—Formula, FoO_3,CaO. This salt is easily obtained pure by supersaturating with milk of lime the impure formic acid prepared by the processes above described from starch or other organic matters. The sulphurous acid which it contains is precipitated as insoluble sulphite of lime, and the excess of lime is removed by a current of carbonic acid. As the salt is hardly more soluble in hot than in cold water, the best way to crystallize it is to evaporate the solution by a gentle heat. During the evaporation it deposits snow-white needles. (Goebel.) It yields very pure formic acid, when distilled with sulphuric acid, more or less diluted.

Formiate of Magnesia. — Formula, FoO_3,MgO. Fine brilliant needles, permanent in the air, soluble in 13 parts of water. (Goebel.)

Formiate of Alumina. — Formula, $3FoO_3,Al_2O_3$. This salt forms, when evaporated, a gummy mass. Its solution is permanent when boiled: if sulphate of potash or alum be added, it becomes turbid when heated, but clears up again on cooling; a property which this salt has in common with the acetate of alumina.

The *Formiates of Manganese*, *Protoxide of Iron*, *Zinc*, *Cadmium*, *Nickel*, and *Cobalt*, are very soluble and crystallizable.

The *Formiate of Cerium* has been described as a white crystalline powder, very sparingly soluble; and it has been proposed to make use of this property for purifying oxide of cerium from other oxides: but the recent discovery of a new metal, *Lantanium*, in the oxide hitherto considered as oxide of cerium, renders it necessary that new researches should be made to ascertain the properties of the salts, both of lantanium, and of cerium when separated from that metal.

Formiate of Copper.—This salt crystallizes in large rhomboidal prisms, very regular, transparent, of a light-blue colour. It effloresces when heated.

Formiate of Lead. — Formula, FoO_3,PbO. When formic acid is added to a saturated solution of acetate of lead, it causes, after a short time, a deposition of brilliant needles of this salt. It is easily obtained from the impure formic acid above mentioned by boiling it with carbonate of lead: the filtered solution deposits, on cooling, crystals of the formiate, which are easily purified by washing with cold water and a second crystallization. This salt requires 36 to 40 parts of cold water for solution, but is much more soluble in hot water. Its sparing solubility affords an easy method of purifying formic acid from acetic acid, the acetate of lead being very soluble. A perfect separation of these two salts may be made by alcohol, in which the formiate of lead is quite insoluble. This salt is used for preparing formic acid, strong or diluted; and also formiate of soda, as above described.

Formiates of Protoxide and Deutoxide of Mercury.—Formula, HgO,FoO_3, and $HgO_2,2FoO_3$. Finely powdered peroxide of mercury dissolves in formic acid at the ordinary temperature, forming a syrupy liquid, which by spontaneous evaporation yields a solid crystalline mass. The slightest heat decomposes this salt; carbonic acid is disengaged, formic acid set free, and formiate of protoxide is generated. This latter salt, when a solution of the former is gently heated, is deposited in brilliant silvery scales, which must be dried by pressure in bibulous paper. When heated, either in the dry state or in solution, this salt is decomposed with a slight explosion in the former case, and effervescence in the latter; carbonic acid and formic acid being set free, and metallic mercury deposited. The following schemes explain these decompositions:—

$$\begin{array}{lcl}
\text{2 at. formiate of deutoxide} & = & C_8H_4O_{16}Hg_2\text{, yield} \\
\cline{3-3}
\text{2 at. formiate of protoxide} & = & C_4H_2O_8\ Hg_2 \\
\text{1 at. hydrated formic acid} & = & C_2H_2O_4 \\
\text{And 2 at. carbonic acid} & = & C_2\quad O_4 \\
\cline{3-3}
 & & C_8H_4O_{16}Hg_2
\end{array}$$

$$\begin{array}{lcl}
\text{Again, 2 at. formiate of protoxide} & = & C_4H_2O_8\ Hg_2\text{ yield} \\
\cline{3-3}
\text{2 at. carbonic acid} & = & C_2\quad O_4 \\
\text{1 at. hydrated formic acid} & = & C_2H_2O_4 \\
\text{2 at. metallic mercury} & = & \qquad\quad Hg_2 \\
\cline{3-3}
 & & C_4H_2O_8\ Hg_2.
\end{array}$$

Formiate of Silver.—Formula, AgO,FoO_3. Prepared by mixing nitrate of silver with an alkaline formiate. It is deposited in shining scales, which are sparingly soluble, and are resolved by heat, like the preceding salt, into carbonic acid, formic acid, and metallic silver.

COMPOUNDS OF FORMULE WITH CHLORINE, BROMINE, AND IODINE.

Chlorine and the hypochlorites act on the chloride, oxide, and hydrated oxide of methule, producing a series of chlorides of formule. As formic acid may be obtained from substances which do not contain formule ready formed, so the chlorides of this radical may be obtained from substances which do not contain it. Thus *perchloride of formule* is a product of the decomposition of chloral by alkalies; and the same compound is produced by distilling alcohol or acetone with hypochlorites. The *perbromide of formule* is obtained in the same way from bromal; and the *periodide of formule* by the action of iodine and potash on alcohol.

When chloride of methule, C_2H_3Cl, is exposed to the rays of the sun in contact with chlorine, three distinct compounds are formed, which have been lately examined by Regnault. (Ann. de Chimie, vol. lxxi. p. 353.) That produced by the first reaction is $C_2H_2Cl_2$. It is a colourless liquid, boiling at 87°. The density of its vapour is 2·94. It is produced from the chloride of methule by the loss of 2 at. hydrogen, which are replaced by 2 at. chlorine. Were the chlorine in this compound replaced by its eq. of oxygen, we should have a hydrated oxide of formule corresponding to aldehyde, the formula of which would be $C_2H_2O_2 = C_2HO, HO$. It would be isomeric or rather polymeric with hydrated acetic acid $= C_4H_4O_4$, and with formiate of methule $= C_2H_3O, C_2HO_3$.

When this chloride is further acted on by chlorine, it is changed into perchloride of formule, C_2HCl_3, while hydrochloric acid is formed. Chloride of methule is converted into perchloride of formule by the aid of 4 at. of chlorine.

$$\left.\begin{array}{l}1\text{ at. MeCl} = C_2H_3Cl\\ 4\text{ at. } \quad Cl = \quad Cl_4\end{array}\right\} = \left\{\begin{array}{l}C_2H\,Cl_3 = 1\text{ at. } FoCl_3\\ \quad H_2Cl_2 = 2\text{ at. } HCl.\end{array}\right.$$

The intermediate compound, $C_2H_2Cl_2$, is converted into perchloride of formule by 2 at. chlorine.

The production of the perchloride of formule from alcohol, pyroxylic spirit, and acetone, is the result of a very complex reaction. When either of these liquids is distilled with hypochlorite of lime, perchloride of formule distils over, while a compound of chloride of calcium and carbonate of lime is deposited in brilliant crystalline grains. The hypochlorite must have an alkaline reaction; if supersaturated with chlorine, the perchloride of formule is not produced. No gas is disengaged, and in particular no carbonic acid is set free. When alcohol is employed, it is probable that chloral is first formed, and that the perchloride of formule is formed by the decomposition of that substance. As the perchloride contains only one-fourth of the carbon contained in the alcohol employed to produce it, the following formulæ probably give a correct explanation of the reaction:—

$$\begin{array}{ll}\text{2 at. alcohol} \quad . \quad . \quad . & C_8H_{12}O_4\\ \text{8 at. hypochlorite of lime} \quad . & \quad O_{16}Cl_8Ca_8\\ \hline & C_8H_{12}O_{20}Cl_8Ca_8\end{array}$$

contain the elements of

1 at. perchloride of formule .	$C_2H \quad Cl_3$
3 at. formiate of lime . .	$C_6H_3\ O_{12}\ Ca_3$
5 at. chloride of calcium .	Cl_5Ca_5
8 at. water	$H_8\ O_8$
	$C_8H_{12}O_{20}Cl_8Ca_8$.

But 3 at. of formiate of lime, in contact with 3 at. of hypochlorite of lime and caustic lime in excess, are converted into 6 at. of carbonate of lime.

It is unnecessary to explain in detail the production of perchloride of formule from oxide of methule, since 4 at. of this substance contain the same elements, and in the same proportions, as 2 at. of alcohol. In like manner, as acetone may be viewed as a compound of 1 at. oxide of acetule, C_4H_3O, and 1 at. oxide of methule, $C_2H_3O = C_6H_6O_2$, the production of perchloride of formule from it may easily be understood.

The periodide of formule is produced by the reaction of 1 at. alcohol with 8 at. iodine, and 6 at. potash; yielding 1 at. periodide of formule, 1 at. formiate of potash, 5 at. iodide of potassium, and 4 at. water.

1 at. alcohol	$C_4H_6O_2$
8 at. iodine	I_8
6 at. potash	$O_6\ K_6$
	$C_4H_6O_8I_8K_6$

are equivalent to

1 at. periodide of formule . .	$C_2H \quad I_3$
1 at. formiate of potash . .	$C_2H\ O_4\ K$
5 at. iodide of potassium . .	I_5K_5
4 at. water	H_4O_4
	$C_4H_6O_8I_8K_6$.

The compounds of iodine, bromine, and chlorine, are all decomposed, although with difficulty, by the alkalies; yielding alkaline formiates and metallic iodides, &c. For example, 1 at. perchloride of formule gives, with 4 at. potash, 1 at. formiate of potash and 3 at. chloride of potassium.

$$\frac{Fo\ |\ O_3+KO}{Cl_3\ |\ K_3.}$$

Protochloride of Formule.—Formula, $C_2HCl = FoCl$. By the action of chlorine on chloride of acetule, Regnault obtained a compound, $C_4H_2Cl_2$, which, if halved, would represent the protochloride of formule. (See Chloride of Acetule.)

Bichloride of Formule. — Formula, $C_2HCl_2 = FoCl_2$. In speaking of the action of chlorine on the compounds of ethule and of acetule, we have already mentioned a substance obtained by Regnault as a product of the action of chlorine on chloride of ethule. This substance may be $C_4H_2Cl_4$, or bichloride of formule, C_2HCl_2.

Perchloride of Formule.—Formula, $C_2HCl_3 = FoCl_3$. (Dumas.) Syn. Chloroform. It is obtained either by distilling chloral with milk of lime, or, as above mentioned, by distilling alcohol, pyroxylic spirit, or acetone, with hypochlorite of lime. The product is mixed with water, which separates the perchloride. It is rectified in the water-bath, dried by digestion with chloride of calcium, and finally distilled with oil of vitriol.

It is a colourless oily liquid, having an agreeable ethereal smell and a sweet taste. Its sp. g. is 1·480, and it boils at about 140°. An alcoholic solution of potash converts it into formiate of potash. (Dumas.) The density of its vapour is 4·2. Calculation gives $\frac{16\cdot465}{4} = 4\cdot116$, representing 4 volumes. It is not altered by distillation with potassium, potash, sulphuric acid, and other acids. When its vapour is passed through a red-hot tube, it is decomposed into carbon, hydrochloric acid, and a crystalline body, which appears in long white needles.

When exposed to the rays of the sun in contact with chlorine, it yields a chloride of carbon, C_2Cl_4, which boils at 173°, and the vapour of which has the density 5·30. (Regnault.) Calculation gives the same number, $\frac{21\cdot209}{4} = 5\cdot30$, representing 4 volumes. This compound may be considered as formic acid in which both the hydrogen and oxygen have been replaced by chlorine, $C_2Cl + Cl_3$. In this point of view it has a great analogy with the sesquichloride of carbon, $C_4Cl_6 = C_4Cl_3 + Cl_3$; which has the same relation to acetic acid, as the chloride of carbon now described has to formic acid. When the chloride, C_2Cl_4, is made to pass through a red-hot tube, it is resolved, according to Regnault, into two new chlorides of carbon, represented by the formulæ $C\ Cl_3$ and $C\ Cl$.

Hydrochlorate of Chloride of Formule. — Formula, $2C_2HCl, HCl$. When chlorine acts on the hydrochlorate of chloride of acetule, this compound is formed along with other products. (Regnault.)

Perbromide of Formule.—Formula, $C_2HBr_3 = FoBr_3$. (Dumas.) Syn. Bromoform. It is prepared exactly as the perchloride, bromine being substituted for chlorine. It resembles the perchloride, but is heavier, having in the liquid form the sp. g. 2·10; and is more easily decomposed by alkalies.

Periodide of Formule.—Formula, $C_2HI_3 = FoI_3$. (Dumas; Mitscherlich.) Syn. Iodoform. Discovered by Serullas, who described it first as a compound of iodine with carburetted hydrogen, and subsequently as iodide of carbon. Mitscherlich also described it as an iodide of carbon; which for some time led to erroneous views of the nature of chloroform, the corresponding compound of chlorine. Dumas first ascertained its true composition. To obtain it, an alcoholic solution of potash is added to an alcoholic solution of iodine, till the latter is decolorized, avoiding all excess of potash. The alcohol is then expelled by gentle evaporation, when the iodide of formule is deposited in crystals, which are purified from iodide of potassium by washing with cold water.

It crystallizes in pale yellow shining scales, having a slight but disagreeable odour, resembling that of saffron, and adhering strongly to the hands, or to substances brought in contact with it. It is insoluble in water; very soluble in alcohol, ether, and pyroxylic spirit. It sublimes at 212°; and at 248° it is decomposed, yielding iodine, carbon, and hydriodic acid. It is rapidly decomposed by an alcoholic solution of potash. Chlorine, with the aid of heat, converts it into perchloride of formule and chloride of iodine. When distilled with chloride of phosphorus or corrosive sublimate, it yields a dark red liquid, sp. g. 1·96, which contains chlorine, iodine, and formule.

Sulphuret of Formule.—Formula, FoS_3? (Bouchardat.) Syn. Sulphoform. When 1 part of periodide of formule is distilled with 3 parts of sulphuret of mercury, there is formed a yellow oily liquid, heavier than oil of vitriol, and insoluble in water. It is converted by an alcoholic solution of potash, into sulphuret of potassium and formiate of potash.

ACTION OF CHLORINE ON THE COMPOUNDS OF METHULE.

Chlorine and Oxide of Methule. — Chlorine decomposes the gaseous oxide of methule with disengagement of hydrochloric acid; and converts it, according to Regnault, into an oily liquid, the formula of which is C_2H_2ClO. This liquid is very mobile, has a suffocating odour, causing a flow of tears, and resembling that of phosgene gas. In a moist air it gives off acid fumes. It may be distilled without change. Its sp. g. is 1·315 at 68°: it boils at

221°. The density of its vapour was found $= 4{\cdot}047$, representing 2 volumes. Calculation gives $\frac{7{\cdot}944}{2} = 3{\cdot}972$. Regnault calls this compound *Monochloruretted Methylic Ether.*

By the further action of chlorine on this compound, Regnault obtained a liquid of a less powerful odour, sp. g. 1·606 at 68°, boiling at 266°. Its formula is C_2HCl_2O. The density of its vapour was found $= 6{\cdot}367$, representing 2 volumes. By calculation it is $\frac{12{\cdot}697}{2} = 6{\cdot}348$. This compound, which Regnault calls *Bichloruretted Methylic Ether*, may be viewed as an oxychloride of formule, corresponding to formic acid in which 2 eq. oxygen are replaced by 2 eq. chlorine, $C_2H\left.\begin{matrix}Cl_2\\O\end{matrix}\right\}$.

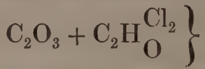
Finally, if the action of chlorine is prolonged, this substance loses all its hydrogen, yielding a very volatile body, C_2Cl_3O, called by Regnault Perchloruretted Methylic Ether. Its odour is strong and penetrating. Its sp. g. is 1·594, and it boils at about 212°. The density of its vapour is 4·670, representing 4 volumes; not 2, like the preceding compounds: by calculation it is $= \frac{17{\cdot}430}{4} = 4{\cdot}36$.

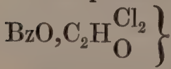
The preparation of these compounds is dangerous, as violent explosions are likely to occur, unless the precautions recommended by Regnault in his memoir (Ann. de Chimie, vol. lxxi. p. 353) are observed.

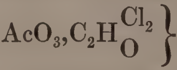
Chlorine and Pyroxylic Spirit.—When chlorine gas is passed through pyroxylic spirit, it is absorbed with evolution of heat and light; and the action is so violent as to cause dangerous explosions, unless the apparatus be screened from light. Towards the end of the operation a gentle heat is required. Two liquids are thus obtained: one aqueous, containing much hydrochloric acid; the other, a heavy oily liquid, which has a pungent taste, and is decomposed by alkalies into formic acid and a new oily liquid. Kane has analyzed the first liquid; but, as the products of its decomposition are not exactly determined, we cannot assign its true formula, nor can we at present explain its formation.

Chlorine and Chloride of Methule.—We have already mentioned, in treating of the chlorides of formule, the conversion of chloride of methule into chloride of formule by the action of chlorine. We have also mentioned that when the perchloride of formule is further acted on by chlorine, with the help of the sun's rays and a gentle heat, chloride of carbon, C_2Cl_4, is obtained. The products of the action of chlorine on chloride of methule are therefore the substance, $C_2H_2Cl_2$, perchloride of formule C_2HCl_3, and the chloride of carbon C_2Cl_4. These compounds are all derived from the chloride of methule, C_2H_3Cl, by the gradual replacement of its hydrogen by chlorine.

Chlorine and Sulphuret of Methule.—According to Regnault, the sulphuret of methule, C_2H_3S, is easily decomposed by chlorine, which converts it into a yellow oily liquid, of a most offensive smell. When the action is complete, the formula of the compound, by an approximative analysis, appears to be C_2Cl_3S; the hydrogen being entirely replaced by chlorine: but, before reaching this point, the reaction seems to yield successively the compounds C_2H_2ClS and C_2HCl_2S.

Chlorine and Oxalate of Methule.—When chlorine is made to act on the oxalate of oxide of methule, several volatile substances are formed: one of which dissolves in water, with disengagement of carbonic acid; and another, when mixed with water, produces oxalic acid, with disengagement of carbonic oxide. Malaguti attributes this last reaction to the decomposition of a substance containing the elements of oxalic acid, chloride of carbon, and water $C_2O_3 + C_2Cl_2 + HO$. The chloride of carbon, in contact with water, produces hydrochloric acid and carbonic oxide. If this compound be represented by the formula  $C_2O_3 + C_2H\left.\begin{matrix}Cl_2\\O\end{matrix}\right\}$ it will be the oxalate of the oxychloride of formule; and its formation is easily explained. The chlorine, acting on the oxide of methule, as formerly explained, produces oxychloride of formule, which unites with the oxalic acid.

Chlorine and Benzoate of Methule.—Chlorine acts on benzoate of oxide of methule; producing, among other products, hydrochloric acid, chloride of benzule, and a compound analogous to the preceding, namely, benzoate of oxychloride of formule,  $BzO,C_2H\left.\begin{matrix}Cl_2\\O\end{matrix}\right\}$. (Malaguti.)

Chlorine and Acetate of Methule.—By the action of chlorine on acetate of oxide of methule, there is formed acetate of oxychloride of formule,  $AcO_3,C_2H\left.\begin{matrix}Cl_2\\O\end{matrix}\right\}$. (Malaguti.) This is a colourless oily liquid, sp. g. 1·25; boiling at about 298°. Water converts it into acetic and hydrochloric acids. Alkalies produce with it formiate and acetate of the alkali, and chloride of the metal.

By distilling a mixture of hydrochloric acid, peroxide of manganese, and pyroxylic spirit, Aimé obtained a yellow oily liquid, which became colourless by washing with water. Of the nature of this liquid nothing is known.

The same chemist has stated that a mixture of pyroxylic spirit, nitric acid, and iodine, left to itself, deposits yellow crystals. If bromine be employed, a heavy oily liquid is formed. Of these compounds nothing further is known.

We are equally destitute of information in regard to the nature of an oily liquid which Aimé has obtained by passing chlorine through a solution of cyanide of mercury in pyroxylic spirit, aiding the reaction by a gentle heat. Without giving the details of his analyses, Aimé has assigned to this substance the formula 2MeO, CyCl; of the accuracy of which there is no evidence.

PRODUCTS OF THE DISTILLATION OF WOOD, OF UNCERTAIN CONSTITUTION.

In the examination of a pyroxylic spirit from a manufactory of pyroligneous acid at Wallwyl, Liebig obtained a colourless inflammable liquid, sp. g. 0·864, having a penetrating ethereal smell and a pungent taste, miscible in all proportions with water. It dissolved chloride of calcium in all proportions, forming a syrupy liquid.

The analyses of this liquid by Liebig and Kane agreed pretty nearly with the formula $C_4H_5O_2$. L. Gmelin obtained results agreeing better with the formula $C_8H_9O_4$; but, as there is no proof of the purity of the liquids analyzed, no certain conclusion can be drawn from these experiments. According to the first formula, this substance might be a compound of 1 at. aldehyde and 2 at. oxide of methule,

$$\begin{array}{l} C_4H_4\ O_2 = \text{hydrated oxide of acetule (aldehyde),} \\ \underline{C_4H_6\ O_2 = \text{2 at. oxide of methule,}\qquad} \\ C_8H_{10}O_4 = 2(C_4H_5O_2)\,; \end{array}$$

or it might contain 3 at. oxide of methule and 1 at. of an oxide of formule corresponding to the oxide of acetule,

$$\begin{array}{l} C_6H_9\ O_3 = \text{3 at. oxide of methule,} \\ \underline{C_2H\ \ O\ \ = \text{1 at. oxide of formule,}\qquad} \\ C_8H_{10}O_4 = 2(C_4H_5O_2). \end{array}$$

One circumstance speaks in favour of the first explanation; namely, that the raw pyroxylic spirit contains free aldehyde, which was extracted from it by Scanlan by means of repeated rectifications. The observation of Scanlan has been confirmed by Liebig, Kane, and Gregory; all of whom obtained aldehydammonia in abundance by the addition of ammonia to the liquid prepared by Scanlan. Moreover, this peculiar pyroxylic spirit, when acted on by potash, gave a thick brown mass very similar to the resin of aldehyde.

Löwig, Weidmann, and Schweitzer, in examining this liquid, found that, when distilled with sulphuric acid and oxalate of potash, it yielded among other products oxalate of methule and acetic acid. Should this observation be confirmed, it will give additional probability to the view according to which it contains aldehyde and oxide of methule.

Adopting the formula $C_8H_9O_4$ or $C_{16}H_{18}O_8$, this liquid, named *Lignone* by Gmelin, might contain acetone, along with a tribasic acetate of methule analogous to acetal, which may be regarded as a tribasic acetate of ethule:

$C_6\,H_9\,O_3$ = 3 at. oxide of methule.
$C_4\,H_3\,O_3$ = 1 at. acetic acid.
$C_6\,H_6\,O_2$ = acetone.
$C_{16}H_{18}O_8$ = lignone.

At all events, lignone appears to contain some compound of oxide of methule.

The raw pyroxylic spirit made in Paris contains, according to L. Gmelin, a certain quantity of acetone.

Berzelius considers lignone as a mixture of pyroxylic spirit and acetate of methule. It is much to be desired that this substance should be thoroughly investigated. Hitherto it has only occurred accidentally in some manufactories, and the circumstances which determine its production are unknown.

CETULE.

Formula, $C_{32}H_{33}$. Symbol, Ct. The hypothetical radical termed *Cetule* combines with 1 at. oxygen to form the *oxide of cetule.* The hydrate of this oxide corresponds to alcohol, and has long been known under the name of *Ethal.* It was discovered by Chevreul, who also detected its analogy to alcohol, and named it from the first syllables of the words ether and alcohol. The researches of Dumas and Peligot have confirmed the opinion of Chevreul. These chemists have produced the chloride of cetule, and the bisulphate of oxide of cetule, belonging to the same series; and we owe to them also the first rational formula for spermaceti, the only substance in which the oxide of cetule has yet been found.

They consider it as a compound of 2 at. margarate of oxide of cetule and 1 at. oleate of oxide of cetule. (See Margaric and Oleic Acids.)

Hydrate of Oxide of Cetule.—Formula, $C_{32}H_{33}O + aq. = CtO = aq.$ (Chevreul, Dumas and Peligot.) Syn. Ethal. Obtained by digesting for some days a mixture of equal parts of spermaceti and fused potash in its own weight of water, at a temperature from 122° to 200°. The soap which is formed is decomposed by diluted sulphuric acid, which separates a fatty mass, composed of margaric and oleic acids and ethal. Having washed it well with boiling water, it is next boiled with an excess of barytic water, which forms insoluble margarate and oleate of baryta. Cold alcohol dissolves out the ethal, which is left when the alcohol is evaporated. It is purified by dissolving it in ether, which separates the last traces of the barytic salts. When the ether is evaporated, pure ethal is left. (Chevreul.)

Dumas and Peligot add powdered potash to melted spermaceti, with continual agitation: combination readily takes place, with the evolution of heat. The mass when cold is treated with water, and decomposed by boiling diluted hydrochloric acid. The oily stratum which separates is subjected a second time to the same operation, that all the spermaceti may be decomposed. The mixture of the fatty acids and ethal is then digested with milk of lime, by which is obtained a mixture of ethal with margarate and oleate of lime. From this the ethal is extracted by cold alcohol, and purified as above.

Ethal forms a solid white crystalline mass, fusible below 118°, and solidifying at that temperature. A boiling alcoholic solution deposits crystalline plates. It may be distilled without change. When heated with water, it volatilizes along with the vapour of water. It is neutral, has neither taste nor smell, and burns like wax. It is insoluble in water, soluble in alcohol and ether. Nitric acid decomposes it. Strong sulphuric acid, with the aid of heat, converts it into bisulphate of oxide of cetule. It does not combine with alkalies.

Chloride of Cetule.—Formula, $C_{32}H_{33}Cl = CtCl$. (Dumas and Peligot.) Obtained by heating ethal with perchloride of phosphorus. It is an oily liquid, the composition of which agrees with the above formula, but its properties have not been particularly examined.

Bisulphate of Oxide of Cetule.—This compound has not yet been obtained in a separate form. It is formed when ethal is heated with sulphuric acid, and the mixture yields double salts. Probable formula, $2SO_3,CtO + aq$.

Double Sulphate of Potash and Oxide of Cetule.—Formula, $2SO_3,CtO,KO$. The mixture of ethal and sulphuric acid is dissolved in alcohol, and neutralized by an alcoholic solution of potash. Sulphate of potash is precipitated, and the double sulphate remains dissolved. It is purified by repeated crystallization, and forms white pearly scales. (Dumas and Peligot.)

PRODUCTS OF THE DECOMPOSITION OF HYDRATE OF OXIDE OF CETULE.

Cetene.—Formula, $C_{32}H_{32}$. (Dumas and Peligot.) Obtained by distilling ethal repeatedly with glacial phosphoric acid, which deprives it of 2 at. water, leaving cetene. It is an oily colourless liquid, insoluble in water, soluble in alcohol and ether. It burns with a smoky flame. It boils at 527°. The density of its vapour was found $= 8·007$, representing 4 volumes. By calculation it is $\frac{31·372}{4} = 7·843$. This compound has the same relation to ethal that olefiant gas, with which it is polymeric, has to alcohol.

AMULE OR AMYLE.

Formula, $C_{10}H_{11}$. Symbol, Ayl. The name of *Amule* or *Amyle* has been given to the hypothetical radical of a series of compounds; one of which, the hydrated oxide of amule, has long been known as the oil of potato spirit. This compound was first analyzed by Dumas, and since minutely investigated by Cahours.

The following are the compounds established by Cahours:—

$C_{10}H_{11} = Ayl$. Amule, unknown in a separate form.
$C_{10}H_{11}O = AylO$. Oxide of amule, unknown in a separate form.
$C_{10}H_{11}O,HO = AylO,aq$. Hydrated oxide of amule, oil of potato spirit.
$C_{10}H_{11}Br = AylBr$. Bromide of amule.
$C_{10}H_{11}I = AylI$. Iodide of amule.
$C_{10}H_{11}O,2SO_3,HO = AylO,2SO_3,aq$. Bisulphate of oxide of amule.
$C_{10}H_{11}O,2SO_3,BaO = AylO,2SO_3,BaO$. Sulphate of baryta and oxide of amule.
$C_{10}H_{11}O,C_4H_3O_3 = AylO,AcO_3$. Acetate of oxide of amule.

Hydrate of Oxide of Amule.—Formula, $C_{10}H_{12}O_2 = C_{10}H_{11}O + HO = AylO + aq$. Syn. Oil of potato spirit; Amilic Alcohol; Bihydrate of Amilene. This compound was first observed by Scheele in the spirit (brandy) obtained from potatoes. It has been examined by Pelletan, Dumas, and Cahours.

When the spirits from potatoes are distilled, there appears, towards the end of the operation, a milky liquid, which, after standing for some time, deposits the oil in question, mixed with water and alcohol. To purify it, it is agitated with water, dried by means of chloride of calcium, and redistilled. As soon as the boiling point rises to 270°, the hydrated oxide of amule distils quite pure. (Cahours.)

It is a colourless liquid, very mobile, but yet oily in appearance. It has a strong smell, which at first is pleasant, but becomes afterwards extremely nauseous. When the vapour is inhaled, it causes asthmatic pains, cough, and even vomiting. Its taste is very acrid. It burns with a bluish-white flame; it boils at 270°; its sp. g. is 0·8124 at 60°. The density of its vapour is $= 3{\cdot}147$, representing 4 volumes. At $-4°$ it solidifies, forming crystalline plates. It produces a stain on paper, which disappears after a short time. It dissolves sparingly in water, to which it communicates its odour; and is miscible in all proportions with alcohol, ether, fixed and volatile oils, and strong acetic acid. It dissolves sulphur, phosphorus, and iodine, without being altered by them. It may also be mixed with solution of caustic potash, or soda, without change; but, when heated with dry potash, hydrogen is disengaged, and valerate of potash is formed (Dumas and Stas). It absorbs a large quantity of hydrochloric acid gas, with evolution of heat. When mixed with oil of vitriol, a violet colour appears, and the bisulphate of oxide of amule is produced. When distilled with dry phosphoric acid, a carbo-hydrogen is obtained, to which Cahours has given the name of *Amilene.* According to Gerhardt, bichloride of tin combines with the hydrated oxide of amule, forming a crystalline compound, which is slowly resolved in the air, and more rapidly when in contact with water, into its component parts—bichloride of tin and hydrated oxide of amule. The chloride of amule has not yet been formed.

Bromide of Amule.—Formula, $C_{10}H_{11}Br = AylBr$. (Cahours.) Syn. Hydrobromate of Amilene. Obtained in the same way as the iodide, next to be described. It is an oily volatile liquid, heavier than water, having an acrid taste and a very penetrating alliaceous smell. It may be distilled without change. An alcoholic solution of caustic potash or soda decomposes it with great facility.

Iodide of Amule.—Formula, $C_{10}H_{11}I = AylI$. (Cahours.) Syn. Hydriodate of Amilene. To prepare this compound, heat is applied to a mixture of 8 parts of iodine, 15 of hydrated oxide of amule, and 1 of phosphorus. The product is washed with water, dried by means of chloride of calcium, and rectified.

It forms a colourless liquid, heavier than water, having a pungent taste and an alliaceous odour. Light decomposes it, setting free iodine. Alkalies act on it as on the preceding compound. The density of its vapour has been found $= 6{\cdot}675$. By calculation it is $\frac{27{\cdot}342}{4} = 6{\cdot}835$.

Bisulphate of Oxide of Amule.—Syn. Sulphoamulic Acid. When the double sulphate of baryta and oxide of amule is dissolved in water, and the baryta separated by sulphuric acid, this compound remains in solution, which may be obtained in the form of a syrupy acid liquid by evaporation in vacuo, and occasionally deposits fine acicular crystals. It has not been obtained, however, in a state of purity. When mixed with alkalies, double salts are formed. If its solution be boiled, it is resolved into free sulphuric acid, which may now be detected by baryta; and hydrated oxide of amule, which separates as an oily stratum.

Sulphate of Potash and Amule.—Formula, $AylO,KO,2SO_3$. Obtained by adding carbonate of potash to the double salt of baryta. It forms white needles, or scales, very soluble in water and in alcohol, and very bitter to the taste.

Sulphate of Baryta and Amule.—Formula of the crystallized salt, $AylO,BaO,2SO_3, + 3aq.$: of the salt dried at 212°, $AylO, BaO,2SO_3 + 2aq.$ To prepare it, equal parts of oil of vitriol and of hydrated oxide of amule are mixed. Combination takes place, attended with production of a violet colour. The mixture is neutralized by carbonate of baryta, which causes a precipitate of sulphate of baryta, while the double salt remains in solution. The solution, after being decolorized by animal charcoal, is evaporated till it crystallizes. The salt appears in pearly scales, very soluble in water and alcohol, and bitter to the taste. Its solution is decomposed by boiling, yielding sulphate of baryta, free sulphuric acid, and hydrated oxide of amule. The dry salt is decomposed by a heat of 392°.

With oxide of lead and with lime, analogous compounds may be formed. The former is represented by the formula $AylO,PbO, 2SO_3 + 2aq.$; the latter by $AylO,CaO,2SO_3 + 2aq.$ The latter appears to be more soluble in cold than in hot water. The solutions of both are decomposed by boiling, exactly like the salt of baryta.

Acetate of Oxide of Amule.—Formula, $C_{10}H_{11}O,C_4H_3O_3 = AylO,AcO_3$. (Cahours.) Syn. Acetate of Amilene. It is easily obtained by distilling a mixture of 2 parts of acetate of potash, 1 of hydrated oxide of amule, and 1 of oil of vitriol. The product, after being dried by means of chloride of calcium, and rectified along with oxide of lead, yields the acetate in a state of purity. It is a colourless liquid, having an ethereal and aromatic odour, insoluble in water, boiling at 248°.

PRODUCT OF THE OXIDATION OF HYDRATED OXIDE OF AMULE.

Valerianic Acid.—Formula, $C_{10}H_9O_3 + aq.$ (Ettling, Dumas, and Stas.) When hydrated oxide of amule is heated along with fused potash, hydrogen is disengaged, and a salt of potash is produced, the acid of which is identical in all respects with that extracted from the root of *Valeriana officinalis* by distilling it with water. To extract the acid from the product of the distillation of the root with water, it is acted on by caustic potash, which separates a volatile oil. By evaporating the mixture this oil is dissipated; and the dry residue, treated with diluted sulphuric acid, and again distilled, yields an aqueous solution of valerianic acid.

When separated from the water, valerianic acid forms a limpid oil, having a strong and offensive smell of valerian. Its sp. g. is 0·944; it boils at 270°, is inflammable, and burns with a white smoky flame. It is miscible in all proportions with alcohol, ether, and oil of turpentine. With bases it forms soluble salts, which have a sweet taste.

The very interesting fact of the formation of this acid by the action of caustic potash on the hydrated oxide of amule was first observed by Dumas. The reaction is exactly analogous to that by which the hyduret of benzule is transformed into benzoic acid; that is, 2 equivalents of hydrogen in the hydrated oxide of amule are replaced by 2 eq. of oxygen.

PRODUCTS OF THE ACTION OF ANHYDROUS PHOSPHORIC ACID AND OF CHLORINE ON THE HYDRATED OXIDE OF AMULE.

A. *Action of Phosphoric Acid.*—When the hydrated oxide of amule is repeatedly distilled with anhydrous phosphoric acid, a colourless liquid is obtained, containing no oxygen, lighter than water, and possessed of a peculiar aromatic odour. This substance, to which Cahours has given the name of *Amilene*, boils at 320°. The density of its vapour was found equal to 5·061. This corresponds to the calculated density: $\frac{9·8038}{2} = 4·90$, if we consider it to represent two volumes according to the formula $C_{10}H_{10}$. It has the same composition in 100 parts as hyduret of acetule (olefiant gas), etherine, and cetene.

B. *Action of Chlorine.*—When a current of chlorine is passed through the hydrated oxide of amule, it blackens, with disengagement of hydrochloric acid gas. When the action is completed, there is obtained a brown oily liquid, heavier than water. To render it neutral, it is washed with a solution of carbonate of soda, and afterwards with water. It boils at 356°, is insoluble in water and in alkalies, soluble in alcohol and ether. These solutions do not cause a precipitate in nitrate of silver till after some time. The analyses of this compound made by Cahours have led him to adopt the formula $C_{20}H_{17}Cl_3O_4$. He has given to it the name of Chloramilal, from a supposed analogy to chloral.

GLYCERULE.

Formula, $C_6H_7 = Gl$. Chemists have long been acquainted with a substance named Glycerine, which is the hydrate of an organic oxide, and which is met with abundantly in nature; forming, in combination with certain acids, the numerous class of solid and liquid bodies known under the name of fats and fixed oils. Glycerule is the hypothetical radical of this oxide. The oxide of glycerule is a compound of this radical with 5 at. oxygen. It is known only in combination with water and acids.

Hydrated Oxide of Glycerule.—Formula, $C_6H_7O_5 + aq$. (Chevreul; Pelouze.) Syn. Glycerine; Sweet Principle of Oils. This substance was discovered by Scheele, who gave it the latter appellation. Chevreul first ascertained its importance, and showed how extensively it occurs. It is to Chevreul and Pelouze that we owe exact experiments in regard to the constitution of this substance.

The hydrated oxide of glycerule is contained in the fatty oils and fats, in combination with oleic, stearic, and margaric acids. To separate it, these bodies are boiled with water and powerful bases, which combine with the acids just mentioned, forming soaps. The newly formed salts are next decomposed by tartaric or sulphuric acid, which separate the oily acids; while an aqueous solution is obtained, containing the alkaline salt along with the glycerine. The mixture is evaporated to dryness, and treated with cold alcohol, which dissolves the glycerine, and leaves the alkaline tartrate or sulphate undissolved.

The most convenient and productive method is to saporify olive oil by means of litharge and a little water. The glycerine is dissolved by the water, and is purified from oxide of lead by a current of sulphuretted hydrogen; while the oxide of lead forms an insoluble soap, or plaster, with the oily acids.

If the solution of glycerine be coloured, it may be decolorized by animal charcoal. It is then evaporated in vacuo over sulphuric acid. When dry, the hydrated oxide of glycerule forms a syrupy liquid, inodorous, but very sweet to the taste. Its sp. g. is from 1·252 to 1·27. It is miscible, in all proportions, with water and alcohol; insoluble in ether. It volatilizes to a slight degree with the vapour of boiling water. It cannot be distilled without decomposition. It is inflammable, burning with a luminous flame.

Nitric acid converts it into oxalic acid; peroxide of manganese with sulphuric acid converts it into formic and carbonic acids. When boiled with sulphate of copper, it reduces the copper to the metallic state. Its solution keeps well, and is not fermentescible.

It combines with sulphuric acid, producing bisulphate of oxide of glycerule. It combines also with potash and baryta; and dissolves, with the aid of heat, the oxide of lead, all deliquescent salts, the sulphates of potash, soda, and copper, and the nitrates of potash and silver.

Chlorine and bromine destroy it; the latter with evolution of heat. When water is added to this mixture, there are obtained an aqueous solution of hydrobromic acid, and a heavy oily liquid, soluble in alcohol and ether, the composition of which is represented by the formula $C_{12}H_{11}O_{10}Br_3$. Gaseous chlorine converts glycerine into a white solid body, $C_{12}H_{11}O_{10}Cl_3$, which has a pleasant ethereal smell, and a taste at once astringent, acid, and bitter.

Bisulphate of Oxide of Glycerule.—Formula, $2SO_3,C_6H_7O_5 +$ aq. Syn. Sulphoglyceric Acid. When 1 part of oil of vitriol is mixed with ½ of glycerine, combination takes place with much evolution of heat, but without blackening. According to Pelouze and Frémy, the same compound is obtained when oils and fats are acted on by oil of vitriol. To obtain it in a state of purity, a solution of the double sulphate of lime and glycerule is carefully precipitated by oxalic acid. It is a very sour liquid, which undergoes spontaneous decomposition, and therefore precipitates the salts of baryta. It is decomposed very rapidly by a gentle heat.

The double salts of glycerule are obtained by adding the bases to the mixture of sulphuric acid and glycerine. These double sulphates are sometimes called sulphoglycerates. Those of lime and baryta are very soluble and crystallizable. When their solutions are boiled, they are resolved into sulphates of the metallic oxides, and hydrated oxide of glycerule.

Sulphate of Lime and Glycerule. — Formula, $CaO,C_6H_7O_5, 2SO_3$. (Pelouze.) Obtained as above described. It forms white needles and scales, soluble in half their weight of water, insoluble in alcohol and ether. At a heat of about 800° it is decomposed, yielding vapours of a very disagreeable smell, which irritate the eyes powerfully. The residue contains carbon and sulphate of lime.

Sulphate of Lead and Glycerule, according to Pelouze, has a composition analogous to that of the preceding salt.

It is probable that the oxide of glycerule exists in nature, combined with other acids besides the fatty acids: such compounds are well worthy of examination. Thus, for example, the benzoate of oxide of glycerule would have the composition of *picrotoxine;* in like manner, mannite may be another oxide of glycerule $= C_6H_7O_6 = GlO_6$.

In the preceding pages of the Organic Chemistry, those substances have been grouped together which stand to each other in a fixed and known relation either with regard to their formation or their composition.

In the remaining part of this work we shall describe those organic compounds concerning the radicals of which nothing certain is yet known.

These compounds will be described in the order of their composition; beginning with those which contain the smallest number of atoms in an equivalent, and going on to those which contain a larger number. In this way, the tribasic acids, or those which in one atom contain the equivalent of three atoms of base, will be first considered. After these will follow the bibasic; and lastly, the monobasic acids. The tribasic and bibasic acids frequently yield pyrogenous acids, or pyro-acids, when decomposed by heat. These will be treated of as products of the decomposition of the acids which yield them.

Many of the compounds now to be described are products of the oxidation of other substances, not acid; these will be noticed in connection with the acids they produce, so that the substances which have a natural connection will be grouped together, as in the case of the substances already described.

MECONIC ACID.

A tribasic acid. Symb. $\overline{\mathrm{Me}}$.

Formula of the anhydrous acid, $C_{14}HO_{11}$ . . $=\overline{\mathrm{Me}}$.
of the acid dried at 212°, $C_{14}HO_{11}+3HO$ $=\overline{\mathrm{Me}}+3aq.$
of the crystallized acid, $C_{14}HO_{11}+3HO+6aq.=\overline{\mathrm{Me}}+9aq.$

Seguin first observed that infusions of opium strike a blood-red colour with persalts of iron. Sertuerner first obtained a meconic acid (pyromeconic acid), by decomposing meconate of baryta with sulphuric acid, and subliming the acid obtained. Robiquet, in 1832, showed that the acid existing in opium differed from the sublimed acid, obtained it in a state of purity, and discovered the komenic acid.

To prepare meconic acid, pure meconate of potash is dissolved in 16 to 20 parts of hot water, and 2 to 3 parts of strong hydrochloric acid are added. On cooling, a quantity of crystals is deposited, chiefly acid meconate of potash; these are treated a second time with water and hydrochloric acid, by which the potash is entirely removed. The crystals should leave no residue when heated on platinum foil. Boiling with hydrochloric or other acids must be avoided, as the acid is thus changed into komenic acid.

Meconic acid forms beautiful pearly scales, of a sour and astringent taste. They lose, when heated, 21 p. c. of water = 6aq. and become opaque. The crystals are sparingly soluble in cold water, much more so in hot water. When the solution is boiled for a long time, the acid is destroyed; and komenic acid, oxalic acid, carbonic acid, and a deep brownish-yellow colouring matter are formed. When boiled with strong hydrochloric acid, komenic and carbonic acids alone are formed. Animal charcoal absorbs meconic acid, and cannot be used to decolorize it. When the acid is exposed to heat, at 248° it is decomposed, yielding water and carbonic acid, while komenic acid is left. If the heat be increased, the komenic acid is resolved into pyromeconic and carbonic acids. Sulphuric acid acts on meconic acid in the same way as hydrochloric acid, but more slowly. Nitric acid decomposes it very rapidly. When boiled with an excess of caustic potash, meconic acid is entirely resolved into oxalic acid, carbonic acid, and a brown matter. (Liebig.) The persalts of iron are coloured of a deep blood-red by meconic acid or its salts. The acid is soluble in alcohol.

MECONATES.

Meconic acid forms with bases three kinds of salts, according as 1, 2, or 3 eq. of the hydratic water are replaced by metallic oxides. The general formulæ for these salts are as follows :

Monobasic Salts.	Bibasic Salts.	Tribasic Salts.
$\overline{\text{Me}},\left.\begin{matrix}\text{MO}\\ 2\text{HO}\end{matrix}\right\}$	$\overline{\text{Me}},\left.\begin{matrix}2\text{MO}\\ \text{HO}\end{matrix}\right\}$	$\overline{\text{Me}},3\text{MO}$.

The only tribasic salt yet analyzed is one formed with oxide of silver. All the soluble monobasic and bibasic meconates have an acid reaction : the soluble tribasic salts have an alkaline reaction. The monobasic and bibasic salts of the alkalies and alkaline earths are sparingly soluble or insoluble : the tribasic are very soluble.

Meconate of Ammonia.—The monobasic and bibasic meconates of ammonia are crystallizable and have an acid reaction. An excess of ammonia produces tribasic meconate, which gives to the liquid a yellow colour.

Meconates of Potash.—$\overline{\text{Me}},2\text{KO},\text{HO}$. The bibasic salt is obtained by adding caustic potash to a mixture of water with the impure meconic acid obtained from the meconate of lime (see below), till a greenish colour begins to appear. Heat is applied till the whole is dissolved; and, on cooling, the salt crystallizes in large quantity. It is purified by pressure, and repeated crystallization. It is sparingly soluble in cold water. Caustic potash added to its solution, produces a soluble tribasic salt which is yellow. If boiled with excess of potash, it is converted into oxalate and carbonate, while an intense colouring matter is formed. If treated with hydrochloric acid, it yields monobasic meconate in shining needles, $=\overline{\text{Me}},\text{KO},2\text{HO}$.

Meconates of Soda.—In all respects analogous to the meconates of potash.

Meconates of Lime.—The insoluble bibasic meconate of lime is easily obtained from opium, by adding chloride of calcium to the infusion of that drug, as in the process of Gregory and Robertson, for preparing muriate of morphia. Its formula is $\overline{\text{Me}},2\text{CaO},\text{HO}+2\text{aq}$. It is used for preparing meconic acid by the following process, which is a modification of Robiquet's, proposed by Gregory. (Ann. der Pharm. xxiv. 43.) One part of this salt is mixed with 20 of water at 212°, and 3 parts of strong hydrochloric acid are added; the whole dissolves, and on cooling deposits monobasic meconate of lime, $\overline{Me}$,CaO,2HO + aq. in silvery crystals. The sulphate of lime, which is always contained in the meconate of commerce in large quantity, is entirely retained in solution by the large excess of hydrochloric acid prescribed; which has also this advantage, that it causes the acid meconate of lime and the meconic acid to crystallize out almost entirely, hardly any being retained in solution. The crystals obtained in the first operation are again treated exactly in the same way, boiling being avoided; and the operation is repeated, if necessary, till the crystals, heated on platinum foil, leave no residue of lime. They are then coloured meconic acid, which is purified by being converted into meconate of potash, as above described; and from the pure meconate of potash the acid is extracted by a similar process, as already mentioned.

The *Meconates* of *Baryta*, *Magnesia*, and *Protoxide of Iron* have been described, but have little interest.

Meconate of Peroxide of Iron.—$\overline{Me}$,Fe_2O_3? This is a very soluble salt, of a deep red colour. Sulphurous acid and protochloride of tin decolorize it, especially with the aid of light. Owing to the intensity of its colour, the persalts of iron may be employed as tests for meconic acid, and hence of opium, the only substance in which meconic acid occurs.

Meconate of Lead.—$\overline{Me}$, 2PbO,HO. A white insoluble powder, sometimes used in preparing meconic acid.

Meconates of Silver. Bibasic.—$\overline{Me}$,2AgO,HO. This salt is obtained by adding nitrate of silver to a solution of meconic acid. It is a heavy, white, insoluble powder. When boiled with water, it forms a yellow tribasic salt, while the water dissolves meconic acid. If heated, it leaves brilliant metallic silver. When boiled with diluted nitric acid, it yields cyanide of silver. (Liebig.)

Tribasic.—$\overline{Me}$,3AgO. Meconic acid, slightly supersaturated with ammonia, gives with nitrate of silver a yellow precipitate of tribasic meconate of silver. (Liebig.)

KOMENIC ACID.

A product of the decomposition of meconic acid. A bibasic acid. Discovered by Robiquet. Formula of the crystallized acid, $C_{12}H_2O_8 + 2HO$. (Liebig.)

Komenic acid is formed from meconic acid, by the influence of heat, or the reaction of a powerful acid. It is also formed by simply boiling meconic acid with water; but in this way it is accompanied by an intense brown colouring matter, formed along with it. When meconic acid is boiled with strong hydrochloric acid, komenic acid is obtained almost colourless. The two acids have a close relation to each other. Meconic acid, containing its basic water, $C_{14}H_4O_{14}$, by losing 2 at. water, 2HO, and 2 at. carbonic acid, $2CO_2$, is converted into komenic acid, $C_{12}H_2O_8$, which takes up 2 at. of basic water.

Komenic acid forms hard crystalline grains, or crusts; its solution decomposes the carbonates, and produces a blood-red colour with the persalts of iron. When heated to 570°, it is resolved into pyromeconic acid, carbonic acid, and water.

KOMENATES.

Komenic acid forms two sets of salts with bases, the general formulæ of which are,

Monobasic Salts.		Bibasic Salts.
$\overline{Ko}+\left.\begin{matrix}MO\\HO\end{matrix}\right\}$	and	$\overline{Ko}+2MO$.

Of these salts little is known; the monobasic alkaline komenates are less soluble than the bibasic salts of the same bases. The monobasic komenate of silver is white, the bibasic yellow. Both have been analyzed by Liebig. (Ann. der Pharm. xxvi.)

PYROMECONIC ACID.

Formula of the crystallized acid, $C_{10}H_3O_5 + aq$. (Robiquet.) It was discovered by Sertuerner, and long viewed as sublimed meconic acid, till Robiquet discovered the meconic acid, from which it is produced.

It is best obtained by distilling komenic acid at 570°. The latter, by losing 1 at. water and 2 at. carbonic acid, yields pyromeconic acid; $C_{12}H_4O_{10} = C_{10}H_3O_5 + HO + 2CO_2$. Towards the end of the distillation, feathery crystals of another acid condense in the neck of the retort, which Gregory considers to be komenic acid, perhaps regenerated. At all events, he found its properties very similar to those of komenic acid.

Pyromeconic acid crystallizes easily, either by sublimation, or from its solution in alcohol. It is very soluble, and strikes a red colour with the persalts of iron. According to Robiquet, it is so feeble an acid that it crystallizes unchanged out of a solution of potash. Its compound with oxide of lead is $C_{10}H_3O_5,PbO$; so that it seems to be a monobasic acid. Liebig has pointed out that its composition is the same as that of pyromucic acid; and thinks it probable that these acids may prove identical. The whole subject requires investigation.

TANNIC ACID.

Formula, $C_{18}H_5O_9 + 3HO$. Symb. $\overline{Qt} + 3aq$. Syn. Tannin; Acidum Quercitannicum.—It is found in every part, but especially in the bark, of all species of quercus, but in the greatest quantity in gall-nuts. To obtain it, coarsely powdered gall-nuts are acted on by ether, which has previously been shaken with water, in a percolator. In the bottle placed below are found two strata of liquid. The heavier is a saturated solution of nearly pure tannic acid in water; the lighter is a solution of gallic acid and of colouring matter in ether. The heavier liquid is gently evaporated to dryness, and leaves a shining porous mass of pure tannic acid. (Pelouze.)

It has usually a pale yellow colour, is very soluble in water, and has a purely astringent taste of singular intensity. It reddens vegetable blues. The solution, when heated in contact with air, absorbs oxygen, giving off an equal volume of carbonic acid, and is converted into gallic and ellagic acids. A moderately strong solution, when mixed with sulphuric, hydrochloric, phosphoric, arsenic, and boracic acids, yields precipitates, soluble in pure water and in alcohol, which are compounds of tannic acid with the other acids. (Berzelius.)

If the compound with sulphuric acid be dissolved with the aid of heat in diluted sulphuric acid, and boiled for a few minutes, the tannic acid disappears, and on cooling a large quantity of coloured crystals of gallic acid is obtained. An analogous change occurs when it is boiled with an excess of caustic alkali. (Liebig.)

Tannic acid combines with the skin of animals, forming an insoluble compound which does not putrefy. This is *leather*. By means of a bit of prepared skin, tannic acid may be entirely withdrawn from its solution in water. A solution of gelatine is precipitated by tannic acid in thick flocks, which dissolve when heated with the supernatant fluid. By the action of heat, tannic acid is converted into metagallic and pyrogallic acids.

TANNATES.

These salts are characterized by striking a deep bluish-black colour with the persalts of iron (*ink*). They do not precipitate gelatine till an acid be added. Tannic acid and the soluble tannates precipitate most of the organic alkalies in the form of white pulverulent compounds, insoluble in water, soluble in acetic acid. A solution of tannic acid, neutralized with potash, yields a thick precipitate, easily soluble in excess of potash; when this alkaline solution is boiled, it produces gallic acid and a brown colouring matter. The cold solution of tannate of potash rapidly absorbs oxygen from the air, and becomes brown.

Ammonia and soda act like potash. The tannates of baryta, strontia, lime, and magnesia are very sparingly soluble. Tannate of alumina is quite insoluble. The salts of protoxide of iron are not altered by tannic acid; but the mixture, when exposed to the air, absorbs oxygen, and becomes black. The black precipitate, formed with the persalts of iron is composed of $3\overline{Qt},Fe_2O_3,9HO$. (Pelouze.)

Tannate of Lead.—When acetate of lead is precipitated by tannic acid, and the precipitate boiled for some time with an excess of the salt of lead, it is changed into a sandy yellow powder, which is neutral tribasic tannate of lead, $\overline{Qt},3PbO$. (Liebig.) The precipitate formed in the cold, according to Berzelius, contains 34·21 p. c. oxide of lead.

Tannic acid produces with a solution of tartar-emetic a white precipitate, $3\overline{Qt},Sb_2O_3$.

The salts of tannic acid require a thorough investigation.

PRODUCTS OF THE DECOMPOSITION OF TANNIC ACID.

It has already been mentioned that tannic acid is readily converted into gallic acid and a brown matter, when boiled with acids or alkalies. The products of the distillation of tannic acid are the same as those of gallic acid; and this circumstance, with some observations of Robiquet, led to the idea that tannic acid contains gallic acid ready formed. An aqueous infusion of nut-galls gradually passes into gallic acid. Hitherto it is impossible to say what is the body which, united with gallic acid, forms tannic acid. According to Braconnot, nut-galls, powdered and moistened, undergo fermentation, yielding alcohol and carbonic acid, which would indicate the presence of sugar, a substance not yet observed in a free state in nut-galls; 3 at. of tannic acid contain the elements of 6 at. of gallic acid and 1 at. of grape sugar.

It is also remarkable that, according to Pelletier, a mixture of gallic acid and gum precipitates gelatine, which neither body separately does.

According to Pelouze, when a solution of tannic acid, by absorbing oxygen, is converted into gallic acid, an equal volume of carbonic acid is given off. If 8 at. oxygen be added to 1 at. tannic acid, we have the elements of 4 at. carbonic acid, 2 at. water, and 2 at. gallic acid, $C_{18}H_8O_{12}+O_8=4CO_2+2HO+2(C_7H_3O_5.)$ According to Erdmann, much ellagic acid is formed in this process. Tannic acid, treated with peroxide of manganese or of lead, is oxidized without the production of gallic acid.

There is reason to think that the brown matter produced when tannic acid is converted into gallic acid by the action of sulphuric acid is a secondary product of the decomposition of a colourless compound produced at first with the gallic acid. If from 1 at. of tannic acid we subtract 2 at. of anhydrous gallic acid, the remainder has the composition of hydrated acetic acid, or of sugar of starch. But acetic acid has been in vain sought for among the products of this reaction; and sugar of starch may be heated with sulphuric acid of the same strength without being decomposed or rendered brown.

The question of the pre-existence of gallic acid in tannic acid is interesting; but it must for the present remain undecided.

GALLIC ACID.

Formula of the crystals, $C_7HO_3+3HO=\bar{G}+3aq.$
of the acid dried at 212°, $C_7HO_3+2HO=\bar{G}+2aq.$
of the acid in the salt of lead, A, $C_7HO_3+HO=\bar{G}+aq.$
in the salt of lead, B, $C_7HO_3=\bar{G}.$

Discovered by Scheele. It exists ready formed in the seeds of the mango, and is a product of the decomposition of tannic acid. Its preparation has been described under tannic acid. The coloured crystals are purified by being combined with oxide of lead, and the compound decomposed by sulphuretted hydrogen. Here the sulphuret of lead acts like animal charcoal in removing the colouring matter.

It crystallizes in brilliant prisms, generally of a pale yellow colour. It is soluble both in water and alcohol, and does not precipitate gelatine. Its solution, exposed to the air, absorbs oxygen, gives off carbonic acid, and becomes brown and mouldy. The presence of alkalies hastens this change. Gallic acid colours the persalts of iron of a deep bluish-black; and forms with solutions of black oxide of iron a permanent black precipitate.

When gallic acid is dissolved in oil of vitriol with the aid of heat, it forms a carmine-red solution, which, when thrown into water, deposits a reddish-brown precipitate, which contains no sulphuric acid, and at 212° loses 10 p. c. water. When thus dried, it is gallic acid minus 1 at. basic water and 1 at. water of crystallization. Its formula is $C_7H_2O_4$. (Robiquet.) This substance is insoluble in water, soluble in alkalies. It may be made to yield the same tints to cloth as madder, with the same mordants. When heated, it yields vermilion-coloured crystals. When gallic acid is heated with a solution of chloride of calcium, carbonic acid is disengaged, and a crystalline powder is deposited, the composition of which is unknown. (Robiquet.)

Heat converts gallic acid into carbonic, pyrogallic, and metagallic acids.

GALLATES.

These salts are distinguished by the rapidity with which they are decomposed when exposed to the air in contact with free alkali. When a little gallic acid is added to an alkaline solution, it passes through yellow, green, red, and brown to black. This colour has sometimes erroneously been attributed to the presence of oxide of iron in mineral waters tested by gallic acid. The only gallates the composition of which is known, are the acid gallate of ammonia, and the gallates of lead.

Acid Gallate of Ammonia is obtained by neutralizing one-half of a solution of gallic acid with ammonia, adding the other half, and crystallizing. It forms short yellowish prisms; the composition of which is, $C_7HO_3,AdH_2O + C_7HO_3,2HO$; or $\bar{G},AdH_2O + \bar{G},HO + aq.$

Acid Gallate of Lead is obtained by adding acetate of lead to a warm solution of gallic acid, leaving an excess of the latter. A white precipitate falls, which, if left in the liquid, changes into a grey crystalline powder. When dried at 212°, it contains $2\bar{G},PbO,HO+aq.$

Basic Gallate of Lead is obtained by adding a solution of gallic acid to a boiling solution of acetate of lead, the latter being in excess. It is a flocculent white precipitate, which when boiled becomes grey and crystalline. Its formula is $\bar{G},2PbO$.

The gallates of potash, soda, and of the protoxides of manganese, iron, zinc, cobalt, and nickel are soluble. The rest are insoluble.

ACTION OF HEAT ON GALLIC AND TANNIC ACIDS.

When tannic acid is distilled by a quick fire, it froths and melts into a black viscid liquid, which, after the heat has been continued for some time, becomes solid. The volatile products are carbonic acid, water, and crystals of pyrogallic acid. The solid residue dissolves in alkalies, and is precipitated by acids as a black powder, which Pelouze calls *Metagallic Acid*, but for which Berzelius proposes the name of *Melangallic Acid.*

When gallic acid is kept for a long time at a heat of 410°, it is changed into a grey powder, which dissolves in hot water, and on cooling yields reddish-coloured crystals of an astringent taste. If gallic acid be heated to 440°, it melts, and leaves a shining black mass, which is soluble in water, and tastes like catechu. It precipitates gelatine; but does not, like tannic acid, precipitate the organic alkalies. At a still higher temperature metagallic acid is formed. The volatile products are the same as those of tannic acid.

PYROGALLIC ACID.

Formula, C_2HO, when reduced to the simplest form. It is uncertain whether its equivalent be $C_6H_3O_3$, or $C_8H_4O_4$. Its preparation by heating tannic or gallic acids has been described.

It forms shining scales or needles, of a bitter and astringent taste; is neutral to test paper, and melts at 240°, boils at 410°, and sublimes unchanged. If suddenly heated to 480°, it is converted into water and metagallic acid; a higher temperature produces carbon and empyreumatic products. It is soluble in water; and reduces gold, silver, and mercury from their solutions. It strikes a bluish-black colour with salts of protoxide of iron, and also with the persalts of iron, which are reduced thereby to protosalts.

Of pyrogallic acid so little is known, that it is even doubtful if it possess acid properties. It stands to gallic acid in the same relation as acetone to acetic acid.

PYROGALLATES.

Of these salts, only the pyrogallate of lead has been examined by Berzelius, Pelouze, and the late R. C. Campbell, of Glasgow. According to the two former, the precipitate formed by adding pyrogallic acid to acetate of lead is $C_6H_3O_3 + PbO$. According to Campbell it is $C_8H_4O_4 + PbO$.

All the salts of pyrogallic acid, in contact with an excess of alkali, undergo a change similar to that of the salts of gallic acid. Pyrogallic acid, neutralized with potash, strikes a deep blue with the persalts, and a bluish-black with the protosalts of iron.

METAGALLIC ACID.

Formula of the anhydrous acid, $C_6H_2O_2$. (Pelouze.) Probable atomic weight, $C_{12}H_3O_3 + HO$.

It is a product of the decomposition of tannic, gallic, and pyrogallic acids, and its preparation has been already described.

It forms a black powder, soluble in alkalies. These solutions have a black colour, and cause black precipitates in solutions of lead and silver. The salt of silver is $C_{12}H_3O_3 + AgO$.

CONSIDERATIONS ON THE FOREGOING FACTS.

Tannic and gallic acids, although of very different composition, yet yield the same products, only in different proportions, by the action of heat; namely, metagallic, pyrogallic, and carbonic acids, and water.

Tannic acid may be viewed as a compound of gallic and pyrogallic acids.

3 at. tannic acid; $3(C_{18}H_8O_{12})$=6 at. gallic acid; $6(C_7H_3O_5)$+2 at. pyrogallic acid, $2(C_6H_3O_3)$.

Now, since gallic acid contains the elements of carbonic and pyrogallic acids, or of carbonic acid, metagallic acid, and water, it is easy to see how all these products may be formed. The proportions, however, differ with the temperature. This renders it difficult to represent all the changes by one simple equation.

It is plain, however, that tannic, gallic, and pyrogallic acids, like the three acids described under meconic acid, have an intimate connection. Further experiments must decide in what form the carbonic and pyrogallic acids exist in the tannic and gallic acids.

NUT-GALLS. ELLAGIC ACID.

From the puncture of an insect (Cynips gallæ tinctoriæ, Olivier) there is produced, on the leaves of all species of quercus, the so-called Nut-galls. These, when of good quality (Aleppo galls), contain 30 to 50 per cent. of soluble matter, chiefly tannic acid.

The alcoholic or aqueous infusion of nut-galls is known by the name of tincture of galls. It contains variable proportions of tannic and gallic acids, and is used as a test.

It precipitates persalts of iron of a deep bluish-black colour; tin, yellowish; nickel, greenish-yellow; cobalt, whitish-yellow; cerium, yellow; copper, grey; titanic acid, red; tellurium, yellow; antimony, white; columbium, reddish-yellow; chromium, brown; molybdenum, brown; lead, white; uranium, reddish-brown; bismuth, reddish; silver, dirty yellow; platinum, dark green; gold, brown; osmium, violet.

A fresh infusion precipitates the salts of cinchonine, quinine, brucine, strychnia, codeine, narcotine, and morphia, all white. These precipitates are soluble in acetic acid.

When the infusion of nut-galls is exposed to the atmosphere, the tannic acid gradually disappears, and is replaced by gallic acid and a insoluble grey powder. Chevreul found that this powder was soluble in alkalies, and precipitated by acids; he called it Ellagic acid (from *Galle* reversed). Braconnot observed, that it is formed in large quantity when nut-galls, moistened, are made to undergo fermentation. It forms with potash a crystallizable salt, insoluble in water, but soluble in alkalies. According to Pelouze, its formula is $C_7H_2O_4 + HO = C_7H_3O_5$, which is the composition of gallic acid dried at 212°. In the anhydrous state it has the same composition as the compound described by Robiquet as produced by the action of sulphuric acid on gallic acid; from which, however, it differs in its colour, and in the insolubility of its compound with potash.

Ellagic acid, when heated, yields a greenish-yellow vapour, which condenses into greenish-yellow crystals, which are soluble without change in sulphuric acid and alkalies, and are dissolved by nitric acid with a red colour, being converted into oxalic acid when the solution is heated for some time.

Grischon has found ellagic acid in the root of tormentilla officinalis.

COMPOUNDS OF UNKNOWN CONSTITUTION SIMILAR IN THEIR RELATIONS TO TANNIC ACID.

Cinchona bark, catechu, and kino, the barks of the pine tribe, and many other vegetables, contain substances analogous to tannic acid, in so far as they are astringent, and are capable of combining with animal skin and gelatine. They differ from it, however, principally in causing a dark green or a grey precipitate with the persalts of iron; for which reason the name of *tannin which precipitates iron green*, and of *tannin which precipitates iron grey*, have been given to them collectively.

The experiments of Geiger, Berzelius, and Waltl tend to prove that the tannic acid in all plants is essentially the same; and that the green and grey colours of the precipitate with salts of iron are owing to the presence of free acid, since the addition of a minute quantity of alkali changes these into the usual bluish-black caused by pure tannic or gallic acids.

CATECHU.

The substance known in commerce under the name of catechu is the dried watery extract of *mimosa catechu*. (Willdenow.) It is astringent and bitter, with a sweetish after-taste. It contains a considerable quantity of tannic acid, soluble in cold water, and very similar in its properties to that from nut-galls. Hitherto, however, it has not been observed to yield when heated the same products as ordinary tannic acid. This modification of tannic acid requires a careful investigation.

CATECHINE.

The portion of catechu which is insoluble in cold water contains a peculiar principle, catechine or tanningenic acid, discovered by Büchner. It is soluble in hot water and in alcohol. The colouring matter dissolved along with it is removed by adding acetate of lead till the liquid becomes colourless, precipitating the lead by sulphate of soda, and allowing the clear liquor to cool, when the catechine is deposited. It can only be safely filtered through paper purified by hydrochloric acid from oxide of iron and lime, as it is coloured by contact with these bases.

Catechine forms a fine white powder composed of silky needles, fusible in a moderate heat, decomposed by a higher temperature. According to Büchner, if heated till it becomes brown, it is changed into tannic acid. It is very sparingly soluble in cold water. Its solution is coloured red by long exposure to the atmosphere, and if now evaporated leaves a red splintery mass, soluble in cold water. Catechine colours green the persalts of iron. It does not precipitate gelatine, tartar-emetic, or vegetable alkalies. According to Svanberg, its formula is $C_{15}H_6O_6$. This requires confirmation.

When exposed to the air in contact with caustic alkalies, it forms black solutions; with carbonated alkalies, red solutions. According to Svanberg, the former contain a new acid, *Japonic Acid*, in combination with the bases; the latter, another new acid, *Rubinic Acid.*

Japonic acid, when separated from its salts, forms a black powder, soluble in hot water. Its formula is $C_{12}H_4O_4 + aq$. That of the japonate of silver is $C_{24}H_8O_8 + AgO$. (Svanberg.) According to this, 2 at. of acid lose 2 at. of water, which are replaced by 1 at. oxide of silver. This is rather improbable.

Rubinic acid has not been obtained in a separate form. Its formula, as it exists in the rubinate of silver, is $C_{18}H_6O_9$. (Svanberg.) The production of these compounds is not yet explained.

According to Pelouze, ether dissolves out of dry catechu a species of tannic acid, the formula of which is $C_{18}H_9O_8$. It remains to be determined whether this is catechine; from which, however, in the present state of our knowledge, it appears to differ in composition.

CITRIC ACID.

A tribasic acid. (Liebig.)

A. Formula in the salt of silver . . . $C_{12}H_5O_{11}=\overline{Ci}$

B. Formula of the acid dried at 212° . $C_{12}H_5O_{11}+3HO=\overline{Ci}+3\ aq.$

C. Formula of the acid crystallized by cooling $C_{12}H_5O_{11}+3HO+aq=\overline{Ci}+4\ aq.$

D. Formula of the acid formed at 61° . $C_{12}H_5O_{11}+3HO+2aq=\overline{Ci}+5\ aq.$

Discovered by Scheele in 1784. It is found in the juice of many fruits, particularly those of the different species of *citrus*, *vaccinium*, and *ribes*.

To obtain it, citrate of lime is formed by adding chalk to lemon juice; and this salt is afterwards decomposed by diluted sulphuric acid in slight excess, and the citric acid purified by crystallization. It is made in large quantity for the calico printers, and for medical purposes, and may be purchased at a cheap rate in a high degree of purity. It is chiefly used in medicine as an ingredient in effervescing powders.

It forms regular transparent crystals, very soluble, of a pleasant acid taste, which differ in the amount of water when formed at different temperatures, as in the above table. The acid D loses two atoms of water at 212°, and is converted into the acid B. The acid C does not lose water, even at 266°. All the modifications melt by heat; and if the heat be removed as soon as other products besides water appear, there is left a transparent deliquescent mass, which is a mixture of citric and aconitic acids. A higher temperature causes the production of carbonic oxide, carbonic acid, acetone, acetic acid, and two pyrogenous acids, with a trifling residue of carbon when the heat has been strong and rapidly applied.

By the action of oil of vitriol, aided by heat, citric acid is resolved into carbonic oxide, carbonic acid, acetic acid, and water, the elements of which it contains.

When melted with an excess of caustic potash, it is resolved into oxalic and acetic acids and water, which is merely a different arrangement of the same elements.

By oxidizing agents in general citric acid is partially converted into acetic acid.

When a few drops of a solution of citric acid are added to lime water, a clear liquid results, which, when heated, deposits a white powder, soluble in acids without effervescence.

CITRATES.

Citric acid forms with bases neutral and basic salts. The formula of the neutral tribasic salts is $\overline{\text{Ci}} + 3\text{MO} + \text{aq.}$, and they correspond to the acid C, its basic water being replaced by an equivalent of protoxide. They contain, besides, 1 at. of water of crystallization, which they lose when heated. Their formula then is $\overline{\text{Ci}} + 3\text{MO}$, corresponding to the acid B.

In the basic salts, either the water of crystallization of the neutral salts is replaced by an equivalent of protoxide, $\overline{\text{Ci}} + 3\text{MO} + \text{MO}$, being thus also analogous to the acid C; or else, in addition to this, they contain 1 at. water of crystallization, $\overline{\text{Ci}} + 3\text{MO} + \left.\begin{matrix}\text{MO}\\\text{HO}\end{matrix}\right\}$, in which case they correspond to the acid D.

The only bibasic citrate yet examined is that of lead, in which 2 of the 3 at. of basic water of the acid D are replaced by oxide of lead.

The citrates, when heated, froth, blacken, and give off an acid liquid.

When an anhydrous citrate, $\overline{\text{Ci}} + 3\text{MO}$, is decomposed by an alcoholic solution of hydrochloric acid, so that each equivalent of citric acid can only obtain 3 eq. water, formed by the oxygen of the oxide, and the hydrogen of the hydrochloric acid, the citric acid resolves itself into hydrated aconitic acid, and the citric acid C; thus,

$$\begin{array}{ll}
\text{3 at. hydrated aconitic acid} & C_{12}H_{6}\,O_{12} = 3(C_{4}\,HO_{3} + \text{aq.}) \\
\text{2 at. citric acid} \quad . \quad . \quad . & \underline{C_{24}H_{18}O_{30} = 2(C_{12}H_{5}O_{11} + 3HO + \text{aq.})} \\
 & C_{36}H_{24}O_{42} = 3(C_{12}H_{5}O_{11} + 3HO.)
\end{array}$$

This is the same change which is produced by heat. (Berzelius.)

Citrate of Ammonia is a very soluble and crystallizable salt, not particularly examined.

Citrate of Oxide of Ethule.—Formula, $\overline{\text{Ci}}, 3\text{AeO}$. (Dumas.) Discovered by Thenard. It is obtained by heating a mixture of citric acid, alcohol, and oil of vitriol, till ether begins to distil over. When the residue in the retort is mixed with water, the citric ether separates as a heavy oily fluid. It is washed with water, dissolved in alcohol, and decolorized by charcoal. The alcohol being dissipated by heat, leaves the new ether pure. It has a faint smell of olive oil, and a bitter taste. Sp. g. = 1·142. It boils at 540°, but is partially decomposed; yielding carbon, pyrocitric acid, and alcohol. It is converted by alkalies into citric acid and alcohol; but is not altered by acids in the cold, nor by chlorine and bromine.

The monobasic and bibasic citrates of ethule are not known. The citrates of methule and glycerule, &c. are also unknown.

Citrate of Potash.—Three citrates of potash exist, $\overline{\mathrm{Ci}},3\mathrm{KO}$; $\overline{\mathrm{Ci}},2\mathrm{KO},\mathrm{HO}$; and $\overline{\mathrm{Ci}},\mathrm{KO},2\mathrm{HO}$. They are soluble and crystallizable, but have not been further investigated.

Citrate of Soda.—Formula of the tribasic salt, $\overline{\mathrm{Ci}},3\mathrm{NaO}$, 11 aq. (Berzelius.) This salt forms large regular crystals. At 212° they lose 7 at. water, leaving $\overline{\mathrm{Ci}},3\mathrm{NaO},4\mathrm{aq}$. When heated to from 360° to 380°, the remaining 4 at. water are expelled; but a portion of the salt is converted into aconitate of soda.

The bibasic salt, $\overline{\mathrm{Ci}},2\mathrm{NaO},\mathrm{HO}$, is obtained by adding to a solution of the last salt half as much citric acid as it already contains. By spontaneous evaporation it forms small prismatic crystals.

The monobasic salt, $\overline{\mathrm{Ci}},\mathrm{NaO},2\mathrm{HO}$, is obtained by a similar process, adding a quantity of citric acid equal to that already present. It forms a gummy amorphous mass; but may be obtained in crystalline grains from an alcoholic solution.

Citrate of Baryta.—Two forms of this salt are known. Citrate of soda added to chloride of barium causes a white precipitate, $\overline{\mathrm{Ci}},3\mathrm{BaO},7\mathrm{aq}$. (Berzelius.) A heat of 300° expels 6 at.; a higher temperature the last atom of water. When a hot solution of citric acid and chloride of barium is added to a hot solution of citrate of soda till the precipitate is dissolved, and the mixture allowed to cool, a crystalline powder is deposited, which contains $2\overline{\mathrm{Ci}},5\mathrm{BaO},\mathrm{HO}+7\mathrm{aq}$. and must be viewed as a compound of the salt first described with a bibasic salt, $\overline{\mathrm{Ci}},2\mathrm{BaO},\mathrm{HO}$.

Citrate of Lime.—The tribasic salt, formed like that of baryta, is $\overline{\mathrm{Ci}},3\mathrm{CaO},4\mathrm{aq}$. (Berzelius.) The precipitate formed by heating citric acid with an excess of lime-water is a basic salt, $\overline{\mathrm{Ci}},3\mathrm{CaO}, + \left.\begin{matrix}\mathrm{CaO}\\ \mathrm{HO}\end{matrix}\right\}$. At 212°, it is converted into $\overline{\mathrm{Ci}},3\mathrm{CaO},\mathrm{CaO}$. The salt formed by adding chalk to lemon or currant juice, from which citric acid is obtained, is a mixture of the two salts just described.

Magnesia, alumina, and protoxide of manganese, each form with citric acid an insoluble tribasic and a soluble monobasic or bibasic salt. The citrate of protoxide of iron is crystallizable; that of the peroxide is brown and soluble. Citrate of zinc is sparingly soluble.

Citrate of Lead.—The tribasic salt, $\overline{\mathrm{Ci}},3\mathrm{PbO},aq.$ is a white powder, resolved, by washing with water, into the soluble bibasic salt, and an insoluble salt with excess of base. The bibasic salt, $\overline{\mathrm{Ci}},2\mathrm{PbO},\mathrm{HO}, + 2aq.$ forms crystalline grains. The basic citrate of lead occurs in two forms; the first is $\overline{\mathrm{Ci}},6\mathrm{PbO}$: the second

$$\left.\begin{matrix}\overline{\mathrm{Ci}},3\mathrm{PbO},\mathrm{PbO}\\ \mathrm{HO}\end{matrix}\right\}.$$

The only citrate of copper yet described is a green crystalline powder, $\overline{\mathrm{Ci}},3\mathrm{CuO},\mathrm{CuO} = \overline{\mathrm{Ci}},4\mathrm{CuO}$. It contains, therefore, an excess of base.

Citrate of Silver forms a brilliant white powder, which, if washed and dried below 60°, is $\overline{\mathrm{Ci}},3\mathrm{AgO},aq.$ When gently heated, it gives off water, and becomes $\overline{\mathrm{Ci}},3\mathrm{AgO}$.

Potash-citrate of Antimony.—This salt, which has properties analogous to tartar-emetic, forms dazzling white prisms. It is composed of $\overline{\mathrm{Ci}},\mathrm{Sb_2O_3} + \overline{\mathrm{Ci}},3\mathrm{KO} + 5aq.$ (Thaulow.) The water is expelled at 375°.

ACTION OF HEAT ON CITRIC ACID.

This subject has occupied the attention of Lassaigne, Dumas, Baup, Robiquet, Dahlström, and Berzelius; but the products vary so much with the circumstances of the experiment, that their results appear contradictory and irreconcileable. The very recent researches, however, of Crasso (Liebig's Annalen, April 1840) have cleared up the whole subject, and reconciled the contradictions of his predecessors. We have only space for his results.

According to Crasso, then, crystallized citric acid, when exposed to heat, exhibits four stages of decomposition. During the first, the water of crystallization alone is given off, and the residue contains unaltered citric acid. The second stage is characterized by white vapours, and the production of acetone, carbonic oxide, and carbonic acid, while the residue consists of hydrated aconitic acid, which is therefore the true pyrocitric acid. In the third stage, the aconitic acid, not being volatile, is itself decomposed, yielding carbonic acid, and an oily liquid, which soon crystallizes. This is the pyroaconitic acid, the citricic acid of Baup, for which Crasso proposes the name of Itaconic acid. In the fourth period, empyreumatic oil is produced, and a voluminous coal remains behind. Crasso has further shown that the aconitic acid, heated by itself, is converted into itaconic acid and carbonic acid; and that the itaconic acid, when heated, yields a volatile acid isomeric with itself, which is identical with the citribic acid of Baup, which he proposes to call Citraconic acid, and which is always more or less formed along with the itaconic acid, owing to the easy decomposition of the latter. The action of heat on citric acid, therefore, gives rise to three distinct acids in regular sequence; 1st, aconitic or pyrocitric acid; 2nd, itaconic or pyroaconitic acid; 3rd, citraconic or pyro-itaconic acid.

ACONITIC ACID.

Formula, $C_4HO_3 + aq.$ Symb. $\overline{At} + aq.$

This acid was discovered by Peschier, in the *aconitum napellus*, and analyzed by L. A. Buchner, jun. The acid observed by Braconnot in *equisetum fluviatile*, and analyzed by Regnault, seems to be identical with it; as does also the acid obtained from citric acid by Berzelius and Dahlstrom, as above described. It is easily extracted from the plants, by combining it with oxide of lead, decomposing the salt by sulphuretted hydrogen, and purifying the acid by solution in ether.

It forms a white crystalline mass, soluble in water, of a pleasant acid taste. It is decomposed by heat, yielding two new acids. Regnault supposed it to be identical with maleic acid; but as the latter is converted by heat into fumaric acid, a change not observed in aconitic acid, this identity is doubtful. It ought to be mentioned also, that the acid from equisetum fluviatile may be sublimed without change, although in all other particulars identical with the acid from aconitum napellus.

Its production is easily explained, for 1 at. anhydrous citric acid, $C_{12}H_5O_{11}$, yields

1 at. aconitic acid $=C_4\ H_2O_4=C_4HO_3+HO.$
1 at. acetone $=C_3\ H_3O.$
4 at. carbonic oxide $=C_4\ \ O_4.$
1 at. carbonic acid $=C\ \ O_2.$
1 at. anhydrous citric acid $=C_{12}H_5O_{11}.$

As above mentioned, this is the true pyrocitric acid.

ACONITATES.

The alkaline aconitates are soluble in water, the others insoluble or sparingly soluble. Their properties are not very interesting. The general formula for these salts is $\overline{At}$,MO. They sometimes contain water of crystallization.

There is some reason to believe that this acid may prove to be tribasic. It will then have the formula $C_{12}H_3O_9 + 3HO$; and the neutral aconitates will have the formula $C_{12}H_3O_9 + 3MO$. Future investigations must determine this point.

ITACONIC ACID.

Syn. Pyrocitric Acid; Citricic Acid. (Baup.) Formula, $C_5H_2O_3 + HO$. Symb. $\overline{It} + aq$.

This acid is obtained, as above mentioned, in the third stage of the distillation of citric acid, or by the action of heat on aconitic acid. It is generally accompanied by some of the acid next to be described, citraconic acid. It may be obtained from the oily mass which distils over, and which commonly crystallizes after a short time, by solution in absolute alcohol, and spontaneous evaporation. The crystals thus obtained, when dissolved in water, yield by slow evaporation large rhomboidal crystals, or octahedrons, soluble in 17 parts of water at 60°.

There is some reason to suppose that it may be a bibasic acid, in which case its formula will be $C_{10}H_4O_6 + 2HO$. In the production of this acid from aconitic acid, 3 at. hydrated aconitic acid, $3(C_4HO_3 + HO) = C_{12}H_6O_{12}$, yield 2 at. carbonic acid, $2CO_2$, and 2 at. itaconic acid, $2(C_5H_2O_3 + HO)$.

ITACONATES.

The neutral itaconates have the general formula $C_5H_2O_3 + MO$, or $C_{10}H_4O_6 + 2MO$. The acid salts are either $2(C_5H_2O_3) + MO + HO$, or $C_{10}H_4O_6 + \left.\begin{matrix} MO \\ HO \end{matrix}\right\}$. They have been studied by Baup and Crasso, to whose memoirs the reader is referred for details.

CITRACONIC ACID.

Syn. Pyrocitric Acid; Citribic Acid. (Baup.) Formula, $C_5H_2O_3 + HO$. Symb. $Ct + aq$.

This acid is formed by the action of heat on itaconic acid, with which it is isomeric. It is volatile, and thus escapes the further action of the heat. It is soluble in less than half its weight of water at 60°, and very soluble in alcohol and ether. It is very probably also a bibasic acid, having the formula $C_{10}H_4O_6 + 2HO$; but this must be determined by future researches.

CITRACONATES.

Citraconic acid forms neutral and acid salts, which have been examined by Crasso. The neutral salts have the general formula $C_5H_2O_3 + MO$, or $C_{10}H_4O_6 + 2MO$. The acid salts are either $2(C_5H_2O_3) + HO + MO$; or $C_{10}H_4O_6 + \left.\begin{matrix} HO \\ MO \end{matrix}\right\}$. It forms with ammoniacal gas a peculiar amorphous compound, which does not contain the water usually present in ammoniacal salts. The formula of this compound is $2(C_5H_2O_3) + NH_3$. When this substance is dissolved in water, and the solution evaporated, it yields crystals of the acid citraconate of ammonia, $2(C_5H_2O_3) + NH_4O + HO$. (Crasso.)

TARTARIC ACID.

A bibasic acid. Formula of the crystallized acid, $C_8H_4O_{10} + 2\,aq.$; of the acid in the bibasic salts, $C_8H_4O_{10} = \bar{T}$. When tartar-emetic dried at 212° is exposed to a stronger heat, it loses water, and there remains in the salt an acid, the formula of which must be $C_8H_2O_8$; but when this salt is redissolved in water, the original acid is reproduced. (Liebig.)

Tartaric acid occurs chiefly in the juice of the grape, but also in many other fruits and parts of vegetables. It was discovered by Scheele, in 1770. It is extracted from the tartar of the grape, which is monobasic tartrate of potash, $\bar{T},KO,HO$, by a process similar to that employed for citric acid, namely, converting it into tartrate of lime, and decomposing this salt by sulphuric acid. It is prepared in large quantity for the calico printers, and for medical use, and is sold in a state of purity at a very low price. Its medical use is the same as that of citric acid. It cannot be easily prepared in the laboratory on a small scale; but a process is given in the Pharmacopœiæ for making it. Tartaric acid forms large transparent, oblique, rhombic prisms, which have a pleasant sour taste. The aqueous solution becomes mouldy by keeping: the solution in alcohol, when heated, is converted into monobasic tartrate of oxide of ethule. When heated, it melts, and yields a variety of new and interesting products.

It contains the elements of 1 at. hydrated acetic acid, and 2 at. hydrated oxalic acid; or of 2 at. hydrated formic acid, and 1 at. anhydrous malic acid. When heated with caustic alkalies, it is resolved into acetic and oxalic acids. (Gay-Lussac.) With hyperoxides it yields formic acid, carbonic acid, and tartrate of protoxide: with diluted sulphuric acid it yields a large quantity of formic acid.

A solution of tartaric acid causes with solutions of caustic lime, baryta, and strontia, white precipitates soluble in excess of acid. It does not precipitate the salts of these earths. It is used as a test for potash and its salts, in which it produces the sparingly soluble monobasic tartrate of potash (cream of tartar). The presence of tartaric acid in the solutions of many metallic oxides prevents their precipitation by alkalies.

TARTRATES.

Tartaric acid forms with bases monobasic and bibasic salts. The former are acid, and have the formula $\overline{T},MO,HO$: the latter are neutral, and their formula is $\overline{T},2MO$. These two eq. of metallic oxides may be different: hence a series of salts with two bases, $\overline{T},\left.\begin{matrix}MO\\mO\end{matrix}\right\}$. With potash and oxide of antimony, tartaric acid forms an important series of compounds. Tartar-emetic contains, for 1 eq. tartaric acid, 1 at. = 3 eq. sesquioxide of antimony, and 1 eq. of potash; it must therefore be viewed as a salt with excess of base. The neutral salt has been lately described. As already mentioned, tartar-emetic at 392°, without blackening, gives off 2 at. water, formed either at the expense of the acid, or by part of the oxygen of the sesquioxide, with hydrogen from the acid. In the latter case it must contain either metallic antimony or a suboxide; but, at all events, it no longer belongs, in this state, to the regular series of the tartrates. When put into water, however, tartar-emetic is reproduced. (Liebig.) At 570° all the tartrates are blackened, and yield a peculiar smell, which is characteristic of this family of salts.

The soluble neutral tartrates become insoluble or sparingly soluble by the addition of tartaric acid; the insoluble or sparingly soluble are rendered soluble by such addition. The tartrates insoluble in water are distinguished by their easy and complete solubility in caustic potash or ammonia.

The tartrates are among the most interesting of organic salts. Our knowledge of them, however, is very far from complete, and a careful study of them will certainly lead to very important results in regard to the true theory of all such combinations.

Tartrate of Ammonia.—*a.* Neutral or bibasic. $\bar{T},2AdH_2O + 2aq.$ (Dulk.) This salt is crystallizable. Its solution, when evaporated, loses ammonia and yields the acid salt. *b.* Acid or monobasic. $\bar{T},AdH_2O,aq.$ (Dulk.) This is a crystalline powder, very soluble in hot, sparingly soluble in cold water. It corresponds to cream of tartar.

Tartrate of Oxide of Ethule. — The neutral or bibasic salt is not yet known. The acid salt, $\bar{T},AeO,aq.$ (Guérin Varry), is produced by heating tartaric acid with alcohol; and may be obtained pure by decomposing the double tartrate of baryta and ethule with sulphuric acid, and evaporating the filtered solution in vacuo. It crystallizes in elongated rhombic prisms, and is very soluble in water and alcohol, insoluble in ether. It is decomposed by heat, with the usual smell of the tartrates. This compound was formerly called tartrovinic acid; it forms with bases double salts, formerly called tartrovinates. It dissolves zinc and iron with disengagement of hydrogen.

Tartrate of Ammonia and Ethule.—$\bar{T},AeO,AdH_2O.$—This salt forms a shining, silky, crystalline and fibrous mass. (Guérin Varry.)

Tartrate of Oxide of Methule.—The acid salt, $\bar{T},MeO,aq.$ is formed in the same way as the tartrovinic acid. It crystallizes in fine needles, and forms a series of double salts. (Guérin Varry.)

Tartrate of Potash.—*a.* Acid or monobasic. Syn. Tartar; Cream of Tartar; Bitartrate of potash. Formula, $\bar{T},KO,HO.$—This important salt occurs in many vegetable juices, but in largest quantity in the juice of the grape; from which it separates in a more or less coloured crystalline crust, as soon as the sugar by fermentation has been converted into alcohol, in which it is insoluble. It is purified by recrystallization, when it forms, on cooling, a crust on the surface of the liquid: hence the name *Cremor tartari.*

It forms hard, opaque, oblique, rhombic prisms, or irregular six-sided prisms. It feels gritty between the teeth, has a faint acid taste, and is permanent in the air. When heated, it melts, froths, gives out the peculiar smell of the heated tartrates, and yields by distillation a solid acid, one of the pyrogenous tartaric acids. It is soluble in 18 parts of boiling water, and in 184 parts at 70°. From its insolubility, it is always formed when an excess of tartaric acid is brought into contact with a salt of potash. Stirring with a glass rod, and the addition of alcohol, hasten its separation. Potash may thus be detected and distinguished from soda.

The purest carbonate of potash (salt of tartar) is obtained by igniting cream of tartar. The residue is the well-known *black flux*, a mixture of charcoal with carbonate of potash; from which water dissolves the carbonate. If made with raw tartar, which contains nitrogen, it is contaminated by cyanide of potassium. When 2 parts of nitre and 1 of tartar are ignited, *white flux* is left, which is nothing else than carbonate of potash; all the charcoal having been oxidized by the nitric acid. Tartar always contains a little tartrate of lime.

Cream of tartar is much used in dyeing, from its power of dissolving metallic oxides. In medicine it is very often used as a laxative and diuretic, and to form an acidulous drink in febrile diseases.

b. Neutral or bibasic.—This salt, the soluble tartar of the pharmacopœia, $\bar{T},2KO$, is easily obtained by adding cream of tartar to a hot solution of carbonate of potash till all effervescence ceases, and the liquid is quite neutral. It forms transparent right rhombic prisms, and has a mild saline, somewhat bitter taste. It is used as a laxative.

Tartrate of Potash and Ammonia.—Syn. Ammoniated Tartar. Formula, $\bar{T},KO,AdH_2O,+aq.$ It is formed by neutralizing cream of tartar with ammonia, and crystallizing the solution. It forms right rhombic prisms, large and transparent; and has a cooling, pungent, saline taste. It is very soluble in water; and the solution when heated loses ammonia, and deposits cream of tartar. It is decomposed by acids in the same way, tartar being deposited. This salt is used in medicine as a laxative, especially on the continent.

Tartrate of Potash and Ethule.—$\bar{\mathrm{T}},\mathrm{KO},\mathrm{AeO},+\mathrm{aq}$. (Guérin Varry.) Obtained by adding a slight excess of sulphate of potash to the double salt of baryta and ethule, and evaporating the filtered solution. It crystallizes in the same form as the preceding salt, being isomorphous with it. Its solution, when heated, is resolved into cream of tartar and alcohol. Guérin Varry mentions another compound of the same ingredients, which has an alkaline reaction, and crystallizes in eight-sided prisms. Its composition is unknown.

Tartrate of Potash and Methule.—$\bar{\mathrm{T}},\mathrm{KO},\mathrm{MeO}+\mathrm{aq}$. (Guérin Varry.) A crystallizable salt, analogous in its mode of formation and in its properties to the foregoing.

Tartrate of Potash and Boracic Acid.—$\bar{\mathrm{T}},\mathrm{KO},\mathrm{BO}_3$. (Duflos.) Syn. Soluble Tartar of the French Pharmacopœia. Cream of tartar and boracic acid, in the proportion of their equivalents, are kept in contact with warm water till all is dissolved, and the liquid then evaporated to dryness. It forms a white amorphous mass, of a sour taste, very soluble in water, insoluble in alcohol. Soubeiran recommends 4 parts of tartar to 1 of boracic acid, which yields $3\bar{\mathrm{T}}+3\mathrm{KO}+\mathrm{BO}_3$. The salt of Duflos is exactly analogous to tartar-emetic; that of Soubeiran to the neutral tartrate of potash and antimony lately discovered. The first salt dissolves a large quantity of cream of tartar, which by evaporation it deposits in crystals. (Duflos.) The solution must not be boiled, otherwise some boracic acid is dissipated. This compound is used as a laxative on the Continent.

Tartrate of Potash and Arsenious Acid.—According to Mitscherlich, this compound may be formed, and is analogous in form and composition to tartar-emetic. Probable formula, $\bar{\mathrm{T}},\mathrm{KO},\mathrm{As}_2\mathrm{O}_3$. The mode of preparing it has not been described.

Tartrate of Soda.—*a.* Acid or monobasic. $\bar{\mathrm{T}},\mathrm{NaO},\mathrm{HO}+2\mathrm{aq}$. (Bucholz.) Formed by adding tartaric acid to the neutral salt. Six-sided prisms, very sour to the taste, very soluble in water. It is used to prepare chlorate of soda from chlorate of potash. When mixed with the latter, eq. to eq., cream of tartar and chlorate of soda are produced—*b.* Neutral or bibasic. $\bar{\mathrm{T}},2\mathrm{NaO},+4\mathrm{aq}$.

Formed by neutralizing tartaric acid with soda. Transparent prisms, permanent in the air, very soluble.

Seidlitz Powders, or Carbonated Effervescing Cheltenham Salts, are an intimate mixture of equal parts of tartaric acid and bicarbonate of soda, in atomic proportions. To these is often added a portion of sulphate of magnesia, or of the tartrate of potash and soda (Rochelle Salt). The powders must be well dried; otherwise they slowly act on each other, and lose the effervescing quality.

Tartrate of Soda and Ethule.—$\bar{T}$,NaO,AeO, + 2aq. (Guérin Varry.) White rhomboidal tables.

Tartrate of Potash and Soda.—$\bar{T}$,KO,NaO + 10aq. (Schulze.) Syn. Rochelle Salt; Salt of Seignette. Formed by neutralizing carbonate of soda with cream of tartar. It forms very large transparent right rhombic, or six, eight, and ten-sided prisms. It has a very mild, hardly saline taste; and may be given in soup or beef-tea in a sufficient dose, without the knowledge of the patient, from its comparative tastelessness. It acts as a laxative, like neutral salts in general.

This salt forms with the tartrate of potash and boracic acid of Duflos a double salt ($\bar{T}$,KO,NaO) + ($\bar{T}$,KO,BO_3). (Duflos.) Syn. Boracic Tartar; Tartarized Borax. One part of borax (biborate of soda) and 3 of cream of tartar are dissolved in 20 of water. The clear portion is evaporated to dryness, and yields a gummy mass, of an acidulous saline taste, deliquescing in the air. The powder, if not very long and carefully dried, and stirred in the drying, has the inconvenience of caking in the bottles in which it is kept, so that it cannot be extracted without breaking them. It is much used in medicine on the Continent.

Tartrate of Lithia.—*a.* Monobasic, $\bar{T}$,LO,HO + 3aq. (Dulk.) *b.* Bibasic, $\bar{T}$,2LO. (Dulk.) The former is crystallizable and very soluble; the latter forms a crystalline mass. Tartrate of lithia and potash, $\bar{T}$,KO,LO, + 2aq. and of lithia and soda, $\bar{T}$,NaO,LO + 4aq. are both soluble and crystallizable. (Dulk.)

Tartrate of Baryta.—$\bar{T}$,2BaO, + 2aq. (Dulk.) A white powder, insoluble in water, soluble in tartaric acid.

Tartrate of Baryta and Ethule.—$\bar{T}$,BaO,AeO, + 2aq. (Guérin Varry.) A solution of tartaric acid in alcohol is first heated, then mixed with water, and neutralized with carbonate of baryta. The filtered liquid yields, by spontaneous evaporation, crystals of this salt, which are soluble in water.

Tartrate of Baryta and Methule.—$\bar{T}$,BaO,MeO,+aq. (Dumas and Péligot.) Analogous to the foregoing salt. It is very soluble in water and crystallizable.

Tartrate of Baryta and Potash, $\bar{T}$,BaO,KO,+2aq. and *Tartrate of Baryta and Soda,* $\bar{T}$,BaO,NaO + 2aq. are both sparingly soluble crystalline powders. (Dulk.)

Tartrate of Strontia. —$\bar{T}$,2SrO + 8aq. (Dulk.) Small four-sided tabular crystals, which lose all their water by a gentle heat or in vacuo.

With strontia, tartaric acid forms a series of double salts, analogous to those above described with baryta.

Tartrate of Lime.—$\bar{T}$,2CaO. This salt, which is formed by neutralizing with the atomic proportion of chalk a boiling solution of cream of tartar, is a white insoluble powder. The filtered liquid, which contains half the tartaric acid in the form of neutral tartrate of potash, yields a quantity of tartrate of lime equal to the first, by the addition of an atom of chloride of calcium. It is from this salt that all the tartaric acid of commerce is obtained, as formerly mentioned.

Of the remaining tartrates, the most important are those of antimony and potash, and of iron and potash, both of which are used in medicine. These will be described; but, in regard to the numerous tartrates and double tartrates which might be enumerated, the salts already described will give a sufficiently clear idea of their constitution, while we cannot here afford space for a detailed account of them.

Tartrate of Potash and Sesquioxide of Antimony.—*a.* With excess of base. Formula, $\bar{T}$,Ko,Sb_2O_3 + 2aq. Syn. Tartar-emetic; Tartarized Antimony. This very important compound is prepared by boiling cream of tartar and finely powdered sesquioxide of antimony, in atomic proportions, with water till all is dissolved. The solution when evaporated deposits octohedral crystals of tartar-emetic. Minute directions for its preparation are given in the Pharmacopœiæ and Dispensatories. Its uses in medicine as an emetic, purgative, diaphoretic, sedative, febrifuge, and counter-irritant, are so well known and important, that it may be truly said that no mineral remedy, except perhaps calomel, is more useful to the practitioner.

When heated to 212°, the crystals become anhydrous. Their formula then is $C_8H_4O_{10}$,KO,Sb_2O_3. But, when heated to 480°, they give off, as already mentioned, 2 at. of water, the elements of which must be derived either from the acid alone, or from the sesquioxide and acid together. Their formula then is $C_8H_2O_8$, KO,Sb_2O_3, or $C_8H_2O_{10},KO,Sb_2O$; or they may contain antimony in the metallic state. It might be supposed that tartaric acid, as it exists in tartrate of silver and tartar-emetic at 212°, $C_8H_4O_{10}$, contains 2 at. of water ready formed, and that the anhydrous acid is really $C_8H_2O_8$. In favour of this view might be adduced the fact that tartar-emetic heated to 480°, when dissolved in water, is restored to its original composition. But not only is it contrary to all analogy to suppose the existence of water ready formed in a salt of silver heated to 212°, such salts being without exception anhydrous; but, moreover, this assumption would lead to many other most improbable conclusions. For the present, therefore, we must consider the tartaric acid, anhydrous, to be $C_8H_4O_{10}$; and we must ascribe the appearance of the 2 at. of water when dry tartar-emetic is heated to 480°, to a partial reduction of the oxide of antimony by the hydrogen of the acid. Liebig considers that a part of the antimony is actually reduced to the metallic state; as above explained, it seems to me possible that a dinoxide may be formed, Sb_2O, which must then be combined with an acid; the formula of which will be $C_8H_2O_{10}$. Such a dinoxide of antimony, however, is unknown. In every view the change produced on tartar-emetic at 480° is most interesting. It occurs in no other salt save tartar-emetic, and hence must be owing to the presence in that salt of an oxide containing 2 at. oxygen more than the usual bases (protoxides). Possibly the same change may occur in the compounds of cream of tartar with boracic acid, arsenious acid, and peroxide of iron; all of which, like sesquioxide of antimony, contain 3 at. oxygen. For a full discussion of this subject I refer to Liebig's paper. (Ann. der Pharm. xxvi. 113.)

b. Neutral Tartrate of Antimony and Potash.—This salt, $3\overline{T},3KO,Sb_2O_3$, is found in the mother-liquid of the crystallization of tartar-emetic, especially where an excess of cream of tartar has been used. It forms small crystals grouped together, but crystallizes with difficulty. By boiling its solution with sesquioxide of antimony, it may be entirely crystallized as tartar-emetic. Hence the importance of having a slight excess of oxide of antimony in the preparation of tartar-emetic. Other salts of tartaric acid, antimony, and potash are found in the same mother-liquid, the nature of which is not yet sufficiently known.

Tartrate of Potash and Sesquioxide of Iron (peroxide of iron).—Syn. Tartarized Iron. This salt is formed, according to the Pharmacopœiæ, by exposing for a long time to the air a mixture of cream of tartar and iron filings moistened with water. A soluble brown compound is gradually formed, the iron absorbing oxygen from the atmosphere. The solution, when evaporated, leaves an amorphous gummy mass, which dissolves readily in water. It might probably be easily formed by digesting cream of tartar with hydrated peroxide of iron. Its probable formula is $\bar{T},KO,Fe_2O_3$: but a neutral compound probably exists, $3\bar{T},3KO,Fe_2O_3$. The tartarized iron is used in medicine.

Tartrate of Lead.—A white insoluble powder, which, when heated in close vessels, leaves a mixture of carbon and metallic lead in a state of minute division, which takes fire spontaneously when exposed to the air. Formula, $\bar{T},2PbO$.

Tartrate of Silver.—$\bar{T},2AgO$. This salt is soluble in hot water, and on cooling crystallizes in silvery scales.

ACTION OF HEAT ON TARTARIC ACID.

This subject has been most ably and minutely investigated by Fremy. (Ann. der Pharm. xxix. 142.) When tartaric acid is heated, with certain precautions, it melts, and gives off one-fourth of its water. It is now deliquescent, and forms soluble salts with lime and baryta, by which means it may be purified from tartaric acid. This new acid, to which Fremy has given the name of *Tartralic Acid*, has, in its salts, the same composition as tartaric acid, but neutralizes one-fourth less base. It differs from tartaric acid, therefore, as pyrophosphoric acid differs from phosphoric acid. The general formula of its salts is, $C_8H_4O_{10}+1\frac{1}{2}MO$; or, more correctly, $C_{16}H_8O_{20}+3MO$.

Tartralate of Lime.—$C_{16}H_8O_{20},3CaO+3aq$. The solution of this salt undergoes spontaneous decomposition, yielding tartrate of lime and free tartaric acid. Thus, 2 at. tartralate of lime, $2(C_{16}H_8O_{20},3CaO+3aq.)$ yield 3 at. tartrate of lime, $3(C_8H_4O_{10},2CaO,+2aq.)$ and 1 at. tartaric acid, $C_8H_4O_{10}$, which takes up 2 at. water from the liquid.

The tartralate of baryta is analogous to that of lime. Tartralate of lead is anhydrous, $C_{16}H_8O_{20},3PbO$.

When tartralic acid is still further heated, it loses more water, and is converted into tartrelic acid, $C_8H_4O_{10} + HO$: this is still the composition of tartaric acid, but with only half the neutralizing power. It corresponds to metaphosphoric acid. Its salts have the general formula, $C_8H_4O_{10},MO$.

The tartrelates of lead, baryta, and lime are anhydrous. In contact with water, the tartrelic acid, as well as the tartralic, passes into tartaric acid, just as happens with the modified phosphoric acids. The tartrelates also, in contact with water, yield tartrates and free tartaric acid; for 2 at. tartrelate of a protoxide, $2(C_8H_4O_{10},MO)$ give 1 at. tartrate, $C_8H_4O_{10},2MO$, and 1 at. tartaric acid, $C_8H_4O_{10}$, which takes 2 at. water from the liquid.

When the heat is raised still further, tartaric, tartralic, and tartrelic acids all lose the whole of their water, and leave anhydrous tartaric acid, $C_8H_4O_{10}$. This is the first instance of an organic acid in the anhydrous state; but it has lost all acid properties, and is quite insoluble in water. This is a powerful argument in favour of the view, according to which all acids are compounds of hydrogen. This inert, insoluble anhydrous tartaric acid, when left long in contact with water, takes up the elements of that fluid by degrees, and passes through the stages of tartrelic and tartralic acids into tartaric acid. According to the hypothesis just alluded to, tartrelic acid will be $C_8H_4O_{11} + H$; tartralic acid, $C_{16}H_8O_{23} + H_3$; and tartaric acid, $C_8H_4O_{12} + H_2$.

By a still higher temperature tartaric acid is decomposed, yielding carbonic acid, water, and two pyrogenous acids, one of which is crystalline, the other oily. The crystalline acid is $C_5H_3O_3 + aq.$ (Pelouze): the oily acid is $C_6H_3O_5 + aq.$ (Berzelius). They are formed from 2 at. tartrelic acid, according to the following equation:

$$2(C_8H_4O_{10},HO)=(C_5H_3O_3,HO)+(C_6H_3O_5,HO)+5CO_2+2HO.$$

For details concerning these acids, I must refer to the original memoirs in the foreign journals.

RACEMIC ACID.

Syn. Paratartaric Acid; Acid of the Vosges. Formula, $C_8H_4O_{10} + 2HO$. Symb. $\bar{R}$. This remarkable acid, which in its parallelism with tartaric acid, affords the most complete and curious example of isomerism, is found in the juice of the grape, particularly in the district of the Vosges, replacing the ordinary tartaric acid. Its composition, as far as our present knowledge extends, is not only the same in 100 parts as that of tartaric acid; but its atomic weight, derived from the analyses of its salts, appears to be exactly the same. Moreover, its salts, although quite distinct from those of tartaric acid, are singularly analogous to them. It cannot be doubted, however, that there must be a real difference in the constitution of these acids, and that this will be discovered as soon as the salts of both acids have been submitted to a minute and thorough investigation. There is nothing yet known, for example, inconsistent with the supposition that racemic acid may be an acid requiring 4 atoms of base to form neutral salts, in which case its formula would be $C_{16}H_8O_{20} + 4HO$.

The crystallized racemic acid contains more water than crystallized tartaric acid. Its formula is $C_8H_4O_{10}, 2HO + 2aq$. The two atoms of water of crystallization are expelled by a heat of about 300°, and the remaining acid has the composition of crystallized tartaric acid. It might be supposed to be anhydrous, and therefore to differ in composition from tartaric acid, were it not that, in combining with bases, with oxide of silver for example, it loses the two atoms of water remaining, which are replaced by metallic oxide.

The action of heat on racemic acid has been studied by Fremy and Berzelius. The former has shown that it yields three compounds, corresponding to those from tartaric acid, and quite analogous to them. These he calls paratartralic, paratartrelic, and anhydrous racemic acid; the composition of which is the same as that of the corresponding products from tartaric acid. Berzelius has found that racemic acid, when distilled, yields the same products as tartaric acid, namely, carbonic acid, water, and the two pyrotartaric acids formerly described.

With potash and sesquioxide of antimony, racemic acid yields a tartar-emetic, distinct in properties from that made with tartaric acid, but identical with it in composition; $\overline{R}, KO, Sb_2O_3$. This salt, when heated to 480° or 500°, undergoes the same curious change as tartar-emetic, giving off 2 at. of water.

The action of racemic acid on alcohol corresponds to that of tartaric acid; and in general its tendency to form salts with two different bases is the same as that of tartaric acid.

These two acids are distinguished by the more sparing solubility of racemic acid, by the force with which it retains its combined water, and by the crystalline form of their salts, which frequently differ in the amount of water of crystallization.

MALIC ACID.

Formula, $C_8H_4O_8 + 2HO$. (Liebig.) Symb. $\bar{M}$. A bibasic acid. This acid is found in many fruits, particularly in the apple. It is most easily obtained from the fruit of sorbus aucuparia (mountain ash or rowan tree) immediately after it has turned red, but while still unripe. The juice is heated to coagulate some albuminous matter, and filtered. It is then nearly neutralized with ammonia, and to 72 parts of juice a solution of 1 part of acetate of lead is added. This causes a precipitate of tartrate and citrate of lead. The filtered liquid is now precipitated by nitrate of lead, and the precipitate allowed to stand in the liquid till it has changed into a mass of crystals. This is well washed, dried, powdered, suspended in water, and decomposed by a current of sulphuretted hydrogen. The filtered liquid is neutralized with ammonia, and decolorized by digestion with animal charcoal. The colourless malate of ammonia is again precipitated by nitrate of lead, and the malate of lead decomposed by sulphuretted hydrogen. By this process Winkler obtained from 296 ounces of juice 19 ounces of pure malate of lead, or upwards of 6 ounces of crystallized malic acid. Liebig recommends converting the first impure solution of the acid into acid malate of ammonia by neutralizing one half, and mixing it with the other. This salt forms large crystals, and is easily obtained colourless.

Malic acid is exceedingly soluble in water, and crystallizes with more difficulty than the foregoing acids. It has a very pleasant acid taste. When exposed to heat, it yields two pyrogenous acids, called by Pelouze, who examined them, maleic and paramaleic acids. They are isomeric, and appear to be identical with two acids found in the vegetable kingdom, namely, equisetic (aconitic?) acid, and fumaric acid.

MALATES.

Malic acid, like tartaric acid, forms neutral or bibasic salts, acid or monobasic salts, and a third class, which are neutral and bibasic, but contain two different bases.

Malate of Ammonia.—The acid or monobasic salt has been described by Liebig. It forms large transparent crystals, resembling white sugar-candy. It is used in the preparation of pure malic acid and malates. Formula, $\bar{M}, AdH_2O, HO$.

Malate of Lime.—a. Bibasic. This salt is formed when malic acid is neutralized by lime water. It is soluble in water when formed, and continues so if dried at the ordinary temperature. Formula, $\bar{M},2CaO + 2aq$. If its solution be boiled, the salt loses 1 at. of water, and becomes $\bar{M},2CaO + aq.$, which is an insoluble salt. The last atom of water is expelled by a heat of nearly 400°, and the anhydrous salt is left, $\bar{M},2CaO$. (Richardson and Merzdorf.)—*b.* Monobasic. This salt is obtained by digesting, in the cold, malic acid with chalk, and gently evaporating the solution, when the acid malate crystallizes. When heated to 390°, it is $\bar{M},CaO,HO$. If heated only to 212°, it is $\bar{M},CaO,HO + 4aq$. If dried at the ordinary temperature, $\bar{M},CaO,HO + 8aq$.

Malate of Baryta.—When a solution of carbonate of baryta is evaporated in vacuo, it yields soluble crystals which are hydrated bibasic malate of baryta, $\bar{M},2BaO + 2aq$. If evaporated at a higher temperature, it deposits a crystalline powder, almost insoluble, which is the anhydrous salt, $\bar{M},2BaO$.

Malate of Lead.—The malic acid has a great tendency to form with lead the monobasic or acid salt. This was first obtained by Donovan, who thought that it contained a new acid, sorbic acid. It forms shining silvery scales. Formula, $\bar{M},PbO,HO$.

Malate of Copper.—According to Richardson and Merzdorf, this salt is a bibasic salt with excess of base. It occurs in three forms: $\bar{M},2CuO,CuO + 6aq.$; $\bar{M},2CuO,CuO + 5aq.$; and $\bar{M},2CuO,CuO + 4aq$. The two former are soluble in water: when their solutions are heated, the latter salt is deposited, which is insoluble.

The malates in general are little known, and require a minute investigation. The composition of the malate of copper differs remarkably from that of the other salts, and renders it probable that the true constitution of malic acid is yet unknown.

ACTION OF HEAT ON MALIC ACID.

When crystallized malic acid is kept for a long time at a temperature a little higher than its melting point, it loses water, and is entirely converted into fumaric or paramaleic acid. But if it be distilled by a very quick fire, it yields a volatile product, which is equisetic or maleic acid, while fumaric acid remains in the retort. These two acids have different properties, but the same composition, in 100 parts, but differ in atomic weight, one being bibasic, and the other monobasic.

MALEIC ACID.

A bibasic acid. Formula, $C_8H_2O_6 + 2HO$. Symbol, $\overline{\text{Ma}}$. When malic acid is distilled with a quick fire, maleic acid passes over with water, in which it is dissolved, and from which it is separated in crystals by evaporation. The crystals are plates, or oblique rhombic prisms, very soluble in water, alcohol, and ether. These solutions have a taste at first sour, afterwards nauseous and metallic. It is distinguished from aconitic acid, which has the same composition, by the action of heat, which resolves it into water and anhydrous maleic acid. If kept for a long time melted at a lower temperature, it gradually passes, like malic acid, into a crystalline mass of fumaric acid. Maleic acid differs from malic acid in containing 2 at. of water less, which sufficiently explains its formation. It was formerly supposed to be identical with equisetic or aconitic acid; but, from the recent researches of Liebig, maleic acid appears to be decidedly bibasic.

The salts of maleic acid are insoluble, or sparingly soluble. The maleate of lead is $\overline{\text{Ma}}, 2PbO + 6aq$. (Pelouze.) There are two maleates of silver: neutral and acid. The former is $\overline{\text{Ma}}, 2AgO$; the latter $\overline{\text{Ma}}, \left.\begin{matrix} AgO \\ HO \end{matrix}\right\}$ (Liebig.)

FUMARIC ACID.

A monobasic acid. Formula, $C_4HO_3 + HO$. Symb. $\overline{\text{Fu}}$. Discovered as a product of the action of heat on malic acid by Lassaigne, and analyzed by Pelouze; in the Fumaria officinalis by Winkler, and in Iceland moss by Schoedler. Demarçay first proved the identity of the acid of the fumaria with that derived from malic acid.

It is best obtained by keeping malic acid for a long time heated a few degrees beyond its melting point, when the liquid is gradually converted into a crystalline mass, from which cold water removes any unchanged malic acid. It is also obtained by heating maleic acid in the same way; and some salts of malic acid, when heated, are converted into salts of fumaric acid.

From the juice of Fumaria officinalis it is precipitated as fumarate of lead by the addition of acetate of lead. The same salt may be obtained from Iceland moss by digesting it with milk of lime, and adding acetate of lead to the filtered solution. The fumarate of lead is then suspended in water, and decomposed by sulphuretted hydrogen. The impure crystals first obtained are purified by solution in hot nitric acid, which on cooling deposits the fumaric acid pure and colourless.

Fumaric acid forms fine soft micaceous scales, soluble in 200 parts of cold water, more soluble in hot water and in alcohol. When heated a small portion sublimes, but the greater part is decomposed.

Fumaramide.—$C_4HO_2 + Ad.$ (Hagen.) Formed by the action of aqua ammoniæ on fumarate of oxide of ethule. A snow-white powder, which is slowly dissolved by long boiling in water. By acids and alkalies it is resolved, like other amides, the elements of water being assimilated, into ammonia and the acid.

The salts of fumaric acid are for the most part crystallizable. It forms with ammonia an acid salt in long prisms, $2\overline{Fu},AdH_2O,HO$. Its salts with the oxides of lead and silver have exactly the same composition in 100 parts as the corresponding salts of maleic acid. Their formulæ are C_4HO_3,PbO, and C_4HO_3,AgO.

ACIDS OF UNKNOWN CONSTITUTION.

The acids now to be described are those whose composition is known, but in regard to which it is uncertain whether they are to be considered as monobasic or polybasic.

KINIC ACID.

Formula of the acid in the basic kinate of lead . $C_7H_4O_4$
,, ,, in the basic kinate of copper $C_7H_5O_5$
,, of the crystallized acid . . . . $C_7H_6O_6$

Kinic acid was discovered in cinchona bark by Hoffmann in 1790. It has since been studied by Henry and Plisson, Baup, Liebig, and Woskresensky, the latter of whom ascertained its true composition.

It is obtained from kinate of lime (a salt which occurs in the manufacture of sulphate of quinine) by the action of diluted sulphuric acid. The sulphate of lime being separated by filtration, the filtered liquid is evaporated to the consistence of syrup, and set aside, when it gradually deposits large crystals of kinic acid, which are oblique rhombic prisms, very similar in appearance to tartaric acid. They are permanent in the air, soluble in 2 parts of water, also in alcohol. Pelletier and Caventon obtained by the distillation of kinic acid a volatile crystalline acid, distinguished by the property of causing a fine green precipitate in salts of peroxide of iron. This acid has not been further examined.

SALTS OF KINIC ACID.

Kinic acid differs from all other organic acids in its relation to bases. According to Woskresensky, it forms four series of salts. In one of its compounds with oxide of lead, 2 at. of basic water are replaced by 2 at. of oxide of lead. This would give for the salt $C_7H_4O_4 + 2PbO$; and for the acid $C_7H_4O_4 + 2HO$. But in the salt called basic kinate of copper, the formula is $C_7H_4O_4 + \left.\begin{matrix}CuO\\HO\end{matrix}\right\}$. Again, the kinate of lime, dried at 248°, contains for 1 eq. of lime a quantity of acid represented by $C_{14}H_{11}O_{11}$; and the kinate of silver is also $C_{14}H_{11}O_{11},AgO$. It is possible that in combining with a larger proportion of the oxides of lead and copper than is equivalent to the base in the salts of lime and silver, the acid has undergone a modification analogous to that which occurs in metaphosphoric or pyrophosphoric acids when they are ignited with excess of base. All the kinates, except that of lead, are soluble. When we compare kinic acid with gallic acid $C_7H_3O_5$, we find that the number of equivalents is the same, but that gallic acid contains 1 eq. of oxygen less, and 1 eq. of hydrogen more. Both acids, according to Berzelius, occur in the bark and soft wood of many trees. *Kinate of lime* occurs ready formed in all kinds of cinchona bark; and when the acidulated infusion is precipitated with excess of lime to obtain quinine or cinchonine, the kinate of lime remains dissolved, and crystallizes when the solution is concentrated to a syrup and set aside.

The other kinates are little known, and the anomalies in their composition have been mentioned above.

PRODUCTS OF THE DECOMPOSITION OF KINIC ACID.

Kinoyle.—When a kinate is distilled, there is obtained, along with the vapour of water, a sublimate in golden-yellow needles. It is obtained easily by heating kinic acid with peroxide of manganese and sulphuric acid. This substance is Kinoyle. It is accompanied by formic acid and other products. (Woskresensky.)

Kinoyle is volatile, and distils unchanged in close vessels. In water it is sparingly soluble; but very soluble in alcohol and ether. Its composition is unknown.

VOLATILE ACIDS OF BUTTER.

In the butter of the cow and goat three volatile acids occur in small quantity, besides the fatty matter which constitutes the chief part of the butter. Chevreul, who discovered these acids, has named them Butyric, Capric, and Caproic acids.

When butter is saponified by boiling with caustic alkalies, and the resulting soap is decomposed by an excess of tartaric acid, certain fatty acids, insoluble in water, are separated. The water retains in solution the tartrate of the alkali, oxide of glycerule, and the volatile acids now under consideration. The solution when distilled yields a product containing the three acids. It is neutralized by hydrate of baryta, and evaporated. The first crystals which are deposited are caprate of baryta; those which crystallize last of all are butyrate of baryta. The intermediate portions are principally caproate of baryta. Butyrate of baryta is soluble in $2\frac{3}{4}$ parts, caproate of baryta in $12\frac{1}{2}$ parts, and caprate of baryta in 200 parts of water. Hence by careful management these three salts may be separated and purified. (Chevreul.)

Hydrated butyric acid is soluble in water in all proportions. The other acids are sparingly soluble, and appear as oils when their salts are decomposed by stronger acids.

BUTYRIC ACID.

Formula of the anhydrous acid . . . $C_8H_5O_3$? (Chevreul.)
,, ,, hydrated acid . . . $C_8H_5O_3+HO$?

Butyrate of baryta is dissolved in water, and the solution decomposed by sulphuric acid, care being taken to leave a little of the salt undecomposed. The filtered liquid when distilled yields a solution of pure butyric acid, from which the water is removed by chloride of calcium. The dried butyric acid appears as a clear oily liquid, with an acid smell of rancid butter, and a pungent acid taste. Sp. g. 0·9765 at 77°. It continues liquid at 16°, evaporates in the air, and boils above 212°.

SALTS OF BUTYRIC ACID.

All the butyrates have a slight smell of the acid. The butyrate of oxide of ethule, however, has a penetrating ethereal smell, like that of old cheese. It is obtained by distilling hydrated butyric acid with alcohol and a little sulphuric acid. (Simon.) It is employed to give to potatoe and grain spirits a flavour like that of rum. Butyrate of oxide of glycerule is an ingredient, in small quantity, of butter. The butyrates of baryta, lime, and lead, are soluble in water, and crystallizable.

According to Löwig, the butyric acid in the dry salt of baryta is $C_7H_6O_3$; and when the salt is distilled, carbonate of baryta is left, and a volatile liquid passes over, which he calls butyrone, and which is $C_6H_6O = C_7H_6O_3 - CO_2$. (Kraus.)? The composition of this acid cannot be considered as determined.

CAPROIC ACID.

It is obtained from the salt of baryta by adding sulphuric acid to its solution, when the caproic acid rises to the surface as an oil, which is dried by chloride of calcium. It is a clear oily liquid, having a sour smell like that of sweat, and a taste at first pungent, afterwards sweetish, like that of apples. Sp. g. 0·922. Liquid at 16°; evaporates in the air; boils at a temperature higher than 212°. It is soluble in 96 parts of water, and miscible with alcohol, ether, and oils. Chevreul's analysis would indicate the formula $C_{12}H_9O_3$ for the anhydrous acid.

The salts of caproic acid are soluble in water, and have the smell of the acid. The caproate of oxide of glycerule exists in butter.

CAPRIC ACID.

Formula of the acid in the caprate of lead, $C_{18}H_{14}O_3$. (Chevreul.) It is obtained from the salt of baryta in the same way as the preceding acid. At 65° it resembles the caproic acid; but at 44° it crystallizes when shaken in fine needles, which remain solid at 60°, and melt entirely when warmed beyond that point. It has a smell like that of caproic acid, but more like that of the goat. It is soluble in water and alcohol.

The caprate of baryta is crystallizable, and requires 200 parts of water for its solution. When a solution of this salt is kept in a stoppered bottle, carbonate of baryta is deposited, and the liquid acquires the smell of the cheese of Roquefort.

Regarding as radical for capric and caproic acid the hyduret of carbon $C_{24}H_{18}$, the numbers from the analysis of caproic acid corresponds to . . . . . . $C_{24}H_{18}+O_6$
capric acid . . . . . $C_{24}H_{18}+O_4$.

HIRCIC ACID.

Composition unknown. Discovered by Chevreul in the fat of the goat. It is prepared from the fat just as the three preceding acids are from butter, and resembles them in appearance, being an oily liquid with an offensive smell of goats.

PHOCENIC ACID.

Syn. Delphinic acid. (Chevreul.)

Formula of the acid in the phocenate of lead $C_{10}H_7O_3$.
„ of the hydrated acid . . . . . . $C_{10}H_7O_3+HO$.

Discovered by Chevreul in train oil, and in the berries of Viburnum opulus. It is prepared from whale or seal oil exactly in the same way as the volatile acids from butter. It forms, when pure, a mobile oily fluid, which has a strong acid smell of train oil and rancid butter, and a pungent acid taste. It is very similar to the preceding acids. It dissolves in 18 parts of water; and the solution, when kept, undergoes decomposition, acquiring the smell of greased leather. Like the preceding acids it is volatile.

The salts of phocenic acid are soluble and crystallizable. Phocenate of baryta forms very large and regular crystals. In vacuo over sulphuric acid it loses 2·41 p. c. water, and the dry salt contains 44 p. c. baryta.

SABADILLIC ACID.

Syn. Cevadic Acid. Discovered by Pelletier and Caventon in the seeds of Veratrium Sabadilla. From the oil which ether extracts from the seeds, the sabadillate of baryta is obtained in the same way as butyrate of baryta from butter. When this salt is heated with concentrated phosphoric acid, the sabadillic acid sublimes in white needles, which are fusible at 70°, and have the smell of butyric acid. Its composition is unknown.

CROTONIC ACID.

Syn. Iatrophic Acid. Discovered by Pelletier and Caventon in the seeds of Croton tiglium. It is obtained from the oil (croton oil) exactly in the same way as the preceding acid. It is solid, very volatile, has a pungent and nauseous smell, a burning taste, and is very poisonous. Croton oil contains some free crotonic acid. The salts of crotonic acid are generally soluble and crystallizable, and have no smell. The composition of the acid is unknown.

CAMPHORIC ACID.

Formula of the anhydrous acid, $C_{10}H_7O_3$. Symb. $\overline{Ca}$. (Malaguti, Laurent, Walter.)

Formula of the hydrated acid, $C_{10}H_7O_3 + HO$. Symb. $\overline{Ca}$, HO. Discovered by Kosegarten. The anhydrous acid was first obtained by Malaguti and Laurent.

To prepare it, camphor is digested with a large excess of nitric acid till it is entirely dissolved, fresh acid being added as often as may be required. The acid solution being evaporated, yields impure camphoric acid. It is purified by combining it with potash, which separates any camphor that may have escaped oxidation. The camphorate of potash is then decomposed by nitric acid, when pure hydrated camphoric acid crystallizes. It forms small scales or needles, of a taste at first sour, then bitter. When distilled, it is resolved into water and anhydrous acid.

The salts of camphoric acid, with the alkalies and alkaline earths, are soluble and crystallizable. The other camphorates are insoluble, or sparingly soluble.

Camphorate of Ammonia. *a.* Neutral. $\overline{Ca},AdH_2O$. *b.* Acid. $3\overline{Ca} + \left.\begin{matrix}2AdH_2O\\HO\end{matrix}\right\} + 9aq.$

Camphorate of Oxide of Ethule. *a.* Acid. $2\overline{Ca}\left.\begin{matrix}AeO\\HO\end{matrix}\right\}$ (Malaguti). Obtained by heating camphoric acid, alcohol, and sulphuric acid together. The addition of water causes the new compound to separate. It is a colourless syrupy liquid, which, by boiling with water, is resolved into camphoric acid, and neutral camphorate of oxide of ethule. It forms with alkalies and bases in general a series of double salts, in which the atom of water is replaced by its equivalent of base.

b. Neutral. The neutral camphorate of oxide of ethule, or camphoric ether, $\overline{Ca},AeO$, is obtained by dissolving in alcohol the product of the distillation of the acid salt. When the alcohol deposits no more crystals of camphoric acid, the addition of water separates the camphoric ether as an oily liquid, sp. g. 1·029. It boils at 545°. Its formula is $\overline{Ca},AeO$. When acted on by chlorine, it yields chlorocamphoric ether, $\overline{Ca},C_4H_3Cl_2O$. (Malaguti.)

The so-called anhydrous camphoric acid, $C_{10}H_7O_3$, is obtained by crystallizing in alcohol the product of the distillation of hydrated camphoric acid, or of the acid camphorate of ethule. It forms long, flat, colourless prisms, which have no sour taste. By very long-continued boiling with water it is dissolved, and passes into hydrated acid. (Laurent.)

The existence of anhydrous organic acids is very doubtful. The substances which are supposed to be so, are in general but imperfectly known. From the action of heat on tartar-emetic, and from the composition of the succinate of lead lately described by Fehling, it appears that the so-called anhydrous tartaric and succinic acids still contain some water capable of being replaced by bases; and, according to Malaguti, the anhydrous camphoric acid forms different salts from the hydrated acid. It is probable that all such acids differ from the common hydrates, in a manner analogous to that in which the modifications of phosphoric acid differ from each other.

Of the salts of anhydrous camphoric acid but little is known; but they are decidedly distinct from the salts of the hydrated acid, and they do not yield the hydrated acid when decomposed by acids, but a gummy mass, which soon hardens, and is soluble in alcohol.

Anhydrous camphoric acid combines with fuming sulphuric acid, with disengagement of sulphurous acid. When the solution is heated, a large quantity of pure carbonic oxide is disengaged, and an acid is left, which, according to Walter, is $C_9H_7O_5S = (C_{10}H_7O_3 + SO_3) - CO$. This explanation does not account for the production of sulphurous acid in the first stage of the process. Walter has analysed the salts of this new acid, but the results are not quite decisive. Probably a purer and more permanent compound might be obtained by the action of the vapour of anhydrous sulphuric acid on anhydrous camphoric acid.

APPENDIX TO CAMPHORIC ACID.

CAMPHOR AND OIL OF CAMPHOR.

In the Camphor-tree of Sumatra and Borneo, *Dryabalanops camphora*, and of Japan, *Persea camphora*, camphor and oil of camphor are found, chiefly in those parts of the wood which in resinous trees contain the resin. The wood is split up, and the solid masses of camphor are taken out. By distilling the wood with water, an additional quantity of camphor is obtained, along with the volatile oil.

Oil of Camphor. — Formula, $C_{20}H_{16}O$ (Martius, Macfarlane). The oil of commerce contains camphor dissolved, which it deposits in crystals by evaporation. By repeated rectification the oil may be obtained colourless: it is a very mobile liquid, refracting light strongly; of sp. g. 0·91. Its boiling point lies above 212°. It absorbs oxygen from the air. By distillation with nitric acid it yields camphor, which differs from it in containing exactly twice as much oxygen. With hydrochloric acid it forms a neutral solid compound, insoluble in water. Oil of camphor dissolves phosphorus, iodine, and sulphur; and is miscible with sulphuric and acetic acids, fixed and volatile oils, ether and alcohol. It forms a stiff jelly with powdered copal.

Camphor.—Formula, $C_{10}H_8O$ (Dumas; Blanchet and Sell). Obtained as above described. According to Dumas, the crystalline substance deposited by oil of lavender is identical with common camphor. Camphor is a white, crystalline, translucent solid, somewhat tough, but easily pulverised when moistened with alcohol. Its sp. g. is 0·9857 to 0·996.* It melts at 347°, and sublimes entirely with ebullition at 400°. The density of its vapour is 5·317. (Dumas.) It evaporates readily in the air. Fragments of camphor, when thrown on water, evaporate more rapidly than when dry, and are thrown into a rotatory motion, arising from the simultaneous formation of the vapours of water and camphor.

---

* A very fine specimen of genuine Borneo camphor, in the possession of Dr. Christison, consists of small fragments heavier than water. This variety of camphor, which has seldom reached Europe, being purchased at an enormous price and highly prized by the Chinese and Japanese, merits a special investigation. Its smell is not exactly the same as that of ordinary camphor, but slightly alliaceous.—W. G.

Camphor is combustible, and burns with a smoky flame. It is soluble in 1000 parts of water, but is said to dissolve easily when boiled with water under increased pressure. Ten parts of alcohol dissolve twelve of camphor. It is also soluble in proof spirit and in ether. The solution in proof spirit (camphorated spirit) is precipitated by water. Fixed and volatile oils, and bisulphuret of carbon, dissolve it. It is miscible by fusion with sulphur and phosphorus. With iodine it forms a brown compound; in chlorine gas it liquefies without apparent decomposition. Oil of vitriol dissolves it; and, when the solution is heated, it yields sulphurous acid gas, and an oil smelling of peppermint and camphor. Nitric acid dissolves camphor, and, when the solution is boiled, it is gradually converted into camphoric acid.

Camphor is used in medicine both internally in the form of emulsion, and externally in the form of ointment. Internally it acts as a diffusible stimulant, but in large doses it is poisonous. It increases the solubility of copal in alcohol, and hence is an ingredient in copal varnish.

Camphrone. — When the vapour of camphor is passed over quicklime at a low red heat, a volatile liquid is obtained among the products, which appears to have the formula $C_{30}H_{21}O$. (Fremy.) This is camphrone. If the same experiment be performed at a white heat, the products are naphthaline, $C_{20}H_8$, olefiant gas, marsh gas, and carbonic oxide gas. (Fremy.)

VALERIANIC ACID.

Formula of the anhydrous acid, $C_{10}H_9O_3$. Symb. $\overline{Va}$. Formula of the hydrated acid, $C_{10}H_9O_3,HO$. Symb. $\overline{Va},HO$. (Ettling; Dumas.)

This acid has already been described as a product of the action of caustic potash on hydrated oxide of amule (oil of potato spirit); and as existing in the root of Valeriana officinalis. (See p. 985.) Besides the hydrated acid above mentioned, there exists another hydrate, $\overline{Va}$,3HO, which is obtained when a strong solution of any of its salts is decomposed by an acid.

The salts of valerianic acid are generally soluble, and have a slight smell of valerian. The valerate of oxide of ethule, $\overline{Va}$,AeO, may be obtained by the action of heat on a mixture of alcohol, oil of vitriol, and valerianic acid. It is an oily liquid, with a penetrating smell of fruit and of valerian; of sp. g. 0·894. (Otto.)

The valerate of oxide of amule, or at least a liquid having the composition $C_{20}H_{20}O_4 = \overline{Va}$,AylO, is obtained by the action of heat on a mixture of oil of vitriol, hydrated valerianic acid, and bichromate of potash. (Dumas and Stass.) It is an oily liquid, which requires a careful investigation. The valerates of metallic oxides are anhydrous, and their general formula is $\overline{Va}$,MO.

ACTION OF CHLORINE ON VALERIANIC ACID.

Chlorovalerisic Acid.—When valerianic acid is acted on in the dark by chlorine gas, a new acid is produced, the formula of which is $C_{10}H_7Cl_3O_4$. If we compare this with hydrated valerianic acid, $C_{10}H_{10}O_4$, it appears that chlorovalerisic acid may be regarded as valerianic acid in which 3 eq. of hydrogen are replaced by 3 eq. of chlorine, without the general character of the compound being changed. The new acid is a viscid liquid, devoid of smell, and is easily soluble in alkalies.

Chlorovalerosic Acid.—When the action of chlorine is assisted by sunlight, another new acid is formed, the formula of which is $C_{10}H_5Cl_4O_3$ in the anhydrous state. It is anhydrous valerianic acid, $C_{10}H_9O_3$, in which 4 eq. of hydrogen have been replaced by 4 eq. of chlorine. Its hydrate is $C_{10}H_5Cl_4O_3 + 3HO$. With bases it forms salts very similar to the salts of valerianic acid. The chlorovalerosate of silver is $C_{10}H_5Cl_4O_3$,AgO.

These very remarkable compounds were discovered by Dumas and Stass. They are good examples of the law of substitution proposed by Dumas, the original type of the compound being retained.

According to Löwig, valerate of lime, when distilled, yields an oily liquid, valerone, $C_9H_9O = C_{10}H_9O_3 - CO_2$. The same chemist states that valerianic acid is in the valerian combined with oxide of glycerule, producing a peculiar fat; but this is doubtful.

ŒNANTHIC ACID.

Formula of the anhydrous acid, $C_{14}H_{13}O_2$. Formula of the hydrated acid, $C_{14}H_{13}O_2,HO$. (Pelouze and Liebig.)

This acid occurs in most fermented liquors, especially in wine and corn spirit, combined with oxide of ethule. When wine is distilled, this compound passes over at the end of the process in small quantity. By digestion with potash, œnanthate of potash is obtained, and from this salt the acid is separated by sulphuric acid, in the form of an oily liquid, which rises to the surface. At 54° it is semi-solid. It has neither taste nor smell; is insoluble in water, soluble in alcohol and ether. In this state it is the hydrated acid. When distilled, it is resolved into water and anhydrous acid.

Of the salts of œnanthic acid only the œnanthate of oxide of ethule is well known. This is the oil obtained by distilling wine or other fermented liquors, at the end of the distillation. It is purified from a little free œnanthic acid by heating it with a weak solution of carbonate of potash, when the pure oil rises to the surface. Its formula is $C_{18}H_{18}O_3 = C_{14}H_{13}O_2 + C_4H_5O$. (Pelouze and Liebig; Mulder.) It is a mobile oily colourless liquid, having a strong smell of wine. Sp. g. 0·862. It boils at 435°. By the action of potash it is resolved into œnanthic acid and alcohol.

It is to be observed, that this singular compound is not the cause of that peculiar fragrance in certain wines which is called the bouquet or aroma; but, on the contrary, of that somewhat unpleasant smell which is found in every kind of wine, and which is so characteristic that we can always tell by it whether a bottle or cask has been used for containing wine, even when the vessel has been for some time empty.

ROCCELLIC ACID.

Formula of the crystallized acid, $C_{17}H_{16}O_4$ (Liebig). Discovered in Roccella tinctoria by Heeren. It is extracted from the lichen by ammonia, and the solution precipitated by chloride of calcium. The roccellate of lime is decomposed by weak hydrochloric acid, when the roccellic acid separates. It is purified by solution in ether and crystallization. It forms fine white needles, fusible about 295°. In its general character it resembles the oily acids. Its salts have been little studied.

VERATRIC ACID.

Formula of the acid in the salt of silver, $C_{18}H_9O_7$. Formula of the hydrated acid, $C_{18}H_9O_7,HO$. (Schrötter.) Discovered by Merck in the seeds of Veratrum Sabadilla. The seeds are exhausted by a mixture of alcohol and sulphuric acid, and the solution precipitated by milk of lime. The veratrate of lime remains in solution. It is decomposed by hydrochloric acid, and the new acid crystallizes. It forms short white transparent prisms, which are soluble in water and alcohol, insoluble in ether. When heated they melt, and are volatilized without residue.

Its salts are for the most part soluble. It forms with oxide of ethule a crystalline compound, $C_{22}H_{14}O_8 = C_{18}H_9O_7 + C_4H_5O$. (Will)

CUMINIC ACID.

Formula of the hydrated acid, $C_{20}H_{11}O_3 + HO$. (Gerhardt and Cahours.) To obtain it, Roman oil of cumin is dropped into melted potash, when hydrogen is disengaged, and cuminate of potash is formed. The addition of an acid causes the cuminic acid to separate. The hydrated acid is a white crystallized solid, which is soluble in alcohol and volatile. Its salts are not known.

According to Gerhardt and Cahours, Roman oil of cumin is a mixture of two oils, one of which is a carbo-hydrogen, and the other analogous to the hyduret of benzule, having the formula $C_{10}H_{11}O_2 + H$. The radical of this oil they call Cumyle $= C_{10}H_{11}O_2$.

According to Völkel the common oil of cumin or caraway, from *Carum carui*, contains two oils, analogous to the foregoing; but his analyses do not agree with the above formula. By the action of the air, or by that of sulphuric acid and bichromate of potash, Roman oil of cumin is converted into cuminic acid.

CARYOPHYLLIC ACID.

Formula uncertain. Discovered by Bonastre in oil of cloves, and first obtained in a state of purity by Ettling. Oil of cloves contains this acid, mixed with an oil, $C_{10}H_8$. The addition of potash separates this oil, while caryophyllate of potash is formed. This salt, distilled with sulphuric acid and water, yields the hydrated acid, which is an oily liquid of sp. g. 1·079, with a strong smell of cloves.

The analyses of this acid, by Böckmann and Ettling, lead to the empirical formula $C_{24}H_{15}O_5$. But a comparison of the salt of baryta with the hydrated acid rather leads to the formula $C_{20}H_{12}O_4 = C_{20}H_{11}O_3 + HO$ for the hydrated acid.

According to Dumas, if the cloves be first treated with alcohol, which dissolves a crystalline substance, caryophylline, and afterwards distilled with water, an acid is obtained, which has the formula $C_{20}H_{13}O_5$, and thus appears to contain 1 at. water more than the acid above mentioned. This latter acid forms with potash an acid salt, which according to Dumas is $C_{40}H_{24}O_{10} + KO$; but which is more probably $C_{40}H_{25}O_9 + KO = 2C_{20}H_{12}O_4 + \left.\begin{matrix}KO.\\HO.\end{matrix}\right\}$

The carbo-hydrogen above mentioned may be supposed to pass into caryophyllic acid by the substitution of 4 eq. oxygen for 4 eq. hydrogen. Thus $2C_{10}H_8 = C_{20}H_{16}$; and $C_{20}H_{16} - H_4 + O_4 = C_{20}H_{12}O_4$.

Alcohol, as above mentioned, extracts from cloves a solid substance, caryophylline, which appears to be closely connected both with the carbo-hydrogen and with the acid. According to Dumas and Ettling, its formula is $C_{20}H_{16}O_2$, or $C_{10}H_8O$, which is identical with that of camphor; from which, however, it differs in being inodorous, and not volatile without decomposition.

The distilled water of cloves deposits another substance in yellowish pearly scales, to which Bonastre has given the name of Eugenine. The analysis of Dumas gives for it the same formula as for caryophyllic acid.

All these substances require to be further studied.

COCOIC ACID.

Formula of the acid in the salt of silver, $C_{27}H_{26}O_3$.

Formula of the hydrated acid, $C_{27}H_{26}O_3 + HO$. (Bromeis.)

This is the crystallizable acid contained in the butter or fat of the cocoa-nut. This fat is white, of the consistence of lard; melts about 70°, and congeals a little above 60°; has an unpleasant cheesy smell and taste, and becomes readily rancid. It is distinguished from most fats by its ready solubility in alcohol.

To obtain the acid, the fat is converted into soap by boiling with an alkali, and the soap decomposed by a mineral acid. The fatty acid mixture obtained is subjected to strong pressure to remove the liquid acid (probably oleic acid), and the pressed cocoic acid is further purified by a second saponification. The soap is repeatedly dissolved in water and separated by the addition of common salt, by which means it is rendered colourless. It is then decomposed by tartaric acid, and the fatty acid crystallized from alcohol till its melting point becomes constant.

It is snow-white, inodorous, and melts at 95°, congealing into a mass like wax. When melted with oxide of lead, it loses 4 eq. water.

With the alkalies it forms salts which are soaps, like the salts of the more common oily acids. The cocoate of oxide of ethule is obtained by passing hydrochloric acid gas into a solution of cocoic acid in alcohol, and adding water. It is a colourless mobile liquid, having a pleasant smell of apples. The cocoate of silver is white and insoluble.

SERICIC ACID.

Syn. Myristic Acid. Discovered by Playfair. Formula of the acid in the salts of baryta and potash, $C_{28}H_{27}O_3$. Formula of the crystallized acid, $C_{28}H_{27}O_3 + HO$. (Playfair.)

This acid exists in combination with oxide of glycerule in the butter of nutmegs, which are the fruit of Myristica moschata. This butter is soluble in 4 parts of hot alcohol, and the solution deposits on cooling silky crystals of sericate of oxide of glycerule (sericine or myristine). From this purified fat the acid is obtained by the usual process for oily acids, as described for the preceding acid. It is purified by repeated crystallization from alcohol or ether.

It forms brilliant white scales of a silky lustre (hence its name), fusible about 120°, and congealing into a crystalline mass. It is soluble in alcohol and ether, and is decomposed by nitric acid, and by heat.

The salts which sericic acid forms with alkalies are distinguished from other soaps by not forming viscid solutions when concentrated, and by not becoming turbid when diluted, as ordinary soaps do. Sericate of oxide of ethule is a colourless mobile liquid, of sp. g. 0·864. Formula, $2\,\overline{\text{Se}} + \left.\begin{matrix}\text{AeO.}\\ \text{HO.}\end{matrix}\right\}$

Sericate of oxide of glycerule, or sericine, exists in the butter of nutmegs. It is purified by washing with alcohol, pressure, and solution in hot ether, from which it crystallizes on cooling. According to Playfair, its formula is $C_{118}H_{113}O_{15} = 4(C_{28}H_{27}O_3) + C_6H_5O_3$. This would give for the oxide of glycerule in this fat the formula $C_6H_5O_3$. Whereas, according to Pelouze, oxide of glycerule is $C_6H_7O_5$. But it is not impossible, as Liebig has suggested, that there may be more than one oxide of glycerule. According to Lecanu, oxide of glycerule is $C_6H_6O_4$; and it will be seen that these three formulæ only differ in the proportion of water. Liebig supposes that these different varieties of glycerine may require different quantities of acid for neutralization, just as some acids are monobasic, others polybasic. He considers stearine a compound of 2 at. stearic acid, 1 at. oxide of glycerule $= C_6H_7O_5$ and 2 at. water; while in sericine, the oxide of glycerule $C_6H_5O_3$, which contains 2 at. of water less, is combined with 2 at. of acid more, 4 at. in all. It has also been supposed by Liebig that oxide of glycerule may be $= C_3H_2O$, in which case the formula of sericine may be $\overline{\text{Se}} + \text{GlyO}$, or possibly $2(\overline{\text{Se}},\text{GlyO}) + 2(\overline{\text{Se}},\text{HO})$. Like all compounds of glycerule, sericine, when distilled, yields the pungent vapour of the substance to be afterwards mentioned, which is called by Berzelius Acroleine. These views are highly ingenious, and promise to throw much light on the constitution of the oils and oily acids; but they require extensive and minute researches to establish them. This subject will be again considered when we come to give a general sketch of these important compounds.

Sericic acid, when heated with potash and a little water, forms a beautiful white soap, which crystallizes out of alcohol. This, as well as the sericate of baryta, is composed according to the general formula $\overline{\text{Se}},\text{MO}$.

Sericate of silver appears to contain water, a rare occurrence in a salt of silver. If so, its formula is $2(\overline{\text{Se}},\text{AgO}) + \text{HO}$. But it is more probably $\overline{\text{Se}},\text{AgO}$.

Sericate of lead, like some other salts of lead, when prepared from the acetate, contains acetate of lead. Its formula is $C_{116}H_{111}O_{15},7PbO = 4(C_{28}H_{27}O_3,PbO) + (\bar{A},3PbO)$.

Playfair, to whom we are indebted for the above and other facts, remarks that sericic acid is not far removed in composition from œnanthic acid. In fact, 2 at. œnanthic acid $= C_{28}H_{26}O_4$ represent 1 at. sericic acid in which 1 eq. of hydrogen has been replaced by 1 eq. of oxygen. It is thus related to œnanthic acid, as hyduret of benzule is to benzoic acid, at least as far as the formulæ are concerned; but no conversion of the one into the other has been observed.

Besides sericine, the butter of nutmegs contains a reddish fat and an aromatic volatile oil. The reddish fat, when distilled, yields, among other products, a black fat, soluble in alcohol and ether. These products have not been further examined.

PALMITIC ACID.

Formula of the acid in the salt of silver, $C_{32}H_{31}O_3$. Formula of the hydrated acid, $C_{32}H_{31}O_3 + HO$. (Fremy, Stenhouse.) Discovered by Fremy in palm oil. To obtain it, the oil is saponified by a caustic alkali, and the soap decomposed by an acid. The oily acid which separates contains some oleic acid, which is removed by solution in alcohol, and by pressure.

In appearance the palmitic acid resembles margaric acid, forming pearly scales. It has also the same melting point, namely 140°. It is saponified by digestion with the carbonated alkalies. It is partly decomposed by distillation. By chlorine it is acted on in a way similar to valerianic acid, yielding a variety of acid oils, in which hydrogen is more or less completely replaced by chlorine, and which retain their chlorine in combining with alkalies.

Palmitine, or palmitate of oxide of glycerule, is the principal solid ingredient of the palm oil or butter. It is purified by pressure, washing with hot alcohol, and finally crystallization from hot ether. It is white and crystalline, very sparingly soluble in hot alcohol, but very soluble in hot ether. It melts at 118°, and congeals to a mass like wax, which is friable. According to Stenhouse, its formula is $C_{35}H_{33}O_4$, which would indicate a compound of 1 at. anhydrous palmitic acid, $C_{32}H_{31}O_3$, united to C_3H_2O; which is the same formula for glycerine as one of those mentioned under the preceding acid as suggested by Liebig. This is possibly derived from ordinary glycerine, $C_6H_7O_5$; for $C_6H_7O_5 - 3HO = C_6H_4O_2 = 2(C_3H_2O)$. Like all the compounds of glycerule, palmitine when distilled yields the penetrating vapours of acroleine.

CETULIC ACID.

Syn. Aethalic Acid. Composition and formula identical with those of palmitic acid, from which, however, it differs in properties. (Dumas and Stass.) Formed by the action of fused potash on ethal (hydrated oxide of cetule). Symbol, $\overline{Cet}$.

The formula of ethal is $C_{32}H_{34}O_2$; that of cetulic acid is $C_{32}H_{32}O_4$. The latter is therefore produced from the former, 2 eq. of hydrogen being replaced by 2 eq. oxygen. The oxygen is derived from the water of the hydrate of potash, so that 4 eq. of hydrogen are set free in the process, 2 from this source, and 2 from the ethal. To prepare the acid, 1 part of ethal is heated with 6 parts of a mixture of fused potash and quicklime in equal proportions, to the temperature of about 425°. Hydrogen is set free, and cetulate of potash is formed. This salt is converted, by means of chloride of barium, into cetulate of baryta, which is purified from ethal by digestion in ether. The cetulate of baryta is decomposed by diluted hydrochloric acid, when cetulic acid is obtained in the form of a fat, fusible at 130°, volatile, insoluble in water, soluble in alcohol and ether. Its salts have the general formula $\overline{Cet},MO$. They have been little studied.

MARGARIC ACID.

Formula of the anhydrous acid, $C_{34}H_{33}O_3$, or $C_{68}H_{66}O_6$. Symb. $\overline{Mr}$. Formula of the hydrated acid, $C_{68}H_{66}O_6 + 2HO$. (Varrentrapp, Redtenbacher, Bromeis, Stenhouse.) Symbol, $\overline{Mr},2HO$. A bibasic acid? Discovered by Chevreul. Syn. Margarulic Acid.

Margaric acid, one of the most widely distributed and most important of the oily acids, is found in combination with oxide of glycerule, (glycerine, sugar of oils,) in several species of animal and vegetable fats and oils, particularly in human fat, in goose fat, and in olive oil, being in these cases mixed or combined with oleate of oxide of glycerule. It is also produced by the action of heat on tallow (stearate of oxide of glycerule) and on stearic acid, and by the oxidation of stearic acid.

The easiest method of obtaining pure margaric acid is to heat hydrated stearic acid with its own weight of nitric acid for some minutes. The fatty acid which separates on cooling is exposed to pressure to remove oleic acid, and purified by repeated crystallization in alcohol, till its melting point becomes constant. It may also be obtained by decomposing pure margarate of lead or of lime by a diluted mineral acid.

Margaric acid has the aspect of a fat, fusible at 140°. Its solution in alcohol has an acid reaction. From ether or alcohol it crystallizes in pearly scales; hence its name.

With bases it forms two series of salts: *a*. Neutral, the general formula of which is $\overline{\text{Mr}} + 2\text{MO}$; *b*. Acid, the general formula of which is $\overline{\text{Mr}} + \left.\begin{matrix}\text{MO}\\ \text{HO}\end{matrix}\right\}$ (Varrentrapp).

SALTS OF MARGARIC ACID.

Margarate of Oxide of Ethule.—$\overline{\text{Mr}}, 2\text{AeO}$. (Varrentrapp.) Prepared by the action of hydrochloric acid gas on an alcoholic solution of margaric acid, and purified by washing with boiling water. It has the appearance of a fat, which melts at about 70°.

The *margarates of potash and soda* are obtained pure by the following method, which we owe to Chevreul. The fat of man, or of the goose, or olive oil, is saponified by boiling with caustic potash or soda. The soaps obtained are decomposed by a mineral acid; and the fatty acid which separates, a mixture of margaric and oleic acids, is heated with 8 parts of water, and potash or soda added till a clear solution is obtained. This solution is then mixed with 50 times its volume of water, which causes the separation of acid margarate of the alkali in pearly scales. These are again dissolved in 8 parts of water, the solution again rendered clear by potash or soda, and again mixed with 50 volumes of water. This operation is repeated till the salt, when decomposed, yields an acid fusible at 140°. The salt is then free from oleate of potash or soda. The acid margarate of potash is $\overline{\text{Mr}}, \left.\begin{matrix}\text{KO}\\ \text{HO}\end{matrix}\right\}$. Heated with as much more potash as it already contains, it yields the neutral salt, $\overline{\text{Mr}}, 2\text{KO}$, which is a regular soap, of a rather soft consistence, soluble both in water and alcohol, but which, when mixed with much water, yields free potash and the acid salt, the latter being insoluble.

The *margarates of soda*, acid and neutral, are quite analogous to those of potash; but the neutral margarate of soda is a somewhat harder soap.

The margarates of baryta, strontia, and lime, are insoluble, white, curdy precipitates. Margarate of lime is easily obtained pure, by dissolving in potash the first half of the products of the distillation of stearic acid, precipitating by chloride of calcium, and boiling the precipitate repeatedly with ether, to remove margarone and a carbo-hydrogen, with which it is contaminated. The purified salt is employed to yield margaric acid.

With oxide of lead, margaric acid forms a neutral, an acid, and a basic salt, all insoluble. The latter is fusible at 212°, and is a true plaster, as the salts of oxide of lead with oily acids commonly are.

Margarate of Oxide of Glycerule.—Syn. Margarine. This compound is unknown in a state of perfect purity, but is the principal ingredient of human fat and of goose fat, combined with the corresponding oleate. It occurs also in a smaller proportion in olive oil, and probably in many other fats and oils. The crystals deposited by a hot alcoholic solution of human fat are a chemical compound of margarate and oleate of glycerule. (Chevreul.) So also are the crystals which form in olive oil when it is exposed to cold. (Pelouze, Boudet.)

The original analyses of Chevreul, which, however, appear to have been made with a margaric acid not quite free from oleic acid, suggest a somewhat different formula from that given above; but the close relation between margaric and stearic acids renders the formula of Varrentrapp more probable. After describing, therefore, stearic acid, we shall give a connected view of these very interesting acids, as far as our knowledge of them at present extends.

STEARIC ACID.

Syn. Hypomargarulic Acid. Discovered in 1811 by Chevreul: Studied by Redtenbacher. Formula of the anhydrous acid, $C_{68}H_{66}O_5$. Symb. $\overline{St}$. Formula of the hydrated acid, $C_{68}H_{66}O_5 + 2HO$. (Redtenbacher.) A bibasic acid?—and the most interesting and important of all the oily acids.

It is best obtained from the stearic acid of commerce, which is used as a substitute for wax in making candles. This commercial acid is prepared by saponifying ox or mutton fat by boiling with potash, precipitating by chloride of calcium, and decomposing the stearate of lime thus formed by a mineral acid. The mixture of stearic and oleic acids thus obtained is freed as far as possible from oleic acid by pressure between warm metallic plates. It thus yields a hard mass like wax. To purify it completely, it is repeatedly crystallized from hot alcohol, till its point of fusion becomes constant at 167°. Stearic acid may also be obtained from the acid stearate of potash, (see that salt,) but still requires to be purified by alcohol, till it acquires the above melting point.

Stearic acid is a firm white solid. When melted, it congeals at 158° into a crystalline mass, which feels greasy, but is pulverizable, and insoluble in water. From alcohol it is deposited in brilliant pearly scales. In the liquid state, at 170°, its sp. g. is 0·854; in the solid state it is 1·01. It is very soluble in ether. It burns like wax, with a clear white flame.

When distilled, it is converted into margaric acid and margarone. Heated with nitric acid, it is first converted into margaric acid; and, by the continued action of nitric acid, the latter is converted into succinic and suberic acids.

STEARIC ACID AND BASES.

As a bibasic acid, stearic acid forms two series of salts. *a.* Neutral. Formula, $\overline{\mathrm{St}},2\mathrm{MO}$.

b. Acid. Formula, $\overline{\mathrm{St}},\left.\begin{matrix}\mathrm{MO}\\ \mathrm{HO}\end{matrix}\right\}$. Stearic acid partially decomposes the alkaline carbonates in the cold, yielding bicarbonate and acid stearate of the alkali. With the aid of heat it expels the carbonic acid entirely, forming a neutral stearate, which is a complete soap, in the case of potash or soda.

Stearate of Ammonia.—Hydrated stearic acid absorbs 2 eq. of ammonia, forming a white inodorous solid. It is soluble in ammonia, but deposits crystals of the acid salt, the formula of which is $\overline{\mathrm{St}},\mathrm{AdH_2O,HO}$. (Chevreul.)

Stearate of Oxide of Ethule.—*a.* Neutral. $\overline{\mathrm{St}},2\mathrm{AeO}$. This is formed, according to Lassaigne, by heating together stearic acid, alcohol, and oil of vitriol. An oily liquid rises to the surface, which solidifies on cooling.—*b.* Acid. $\overline{\mathrm{St}},\left.\begin{matrix}\mathrm{AeO}\\ \mathrm{HO}\end{matrix}\right\}$. When hydrochloric acid gas is passed through an alcoholic solution of stearic acid, this compound separates. It resembles wax, and melts between 80° and 90°. It crystallizes from alcohol, and is decomposed by boiling with potash, yielding stearic acid and alcohol. (Redtenbacher.)

Stearate of Oxide of Methule, neutral, according to Lassaigne, is formed like the neutral compound of ethule, which it resembles.

Stearate of Oxide of Glycerule.—This compound, the stearine of Chevreul and Lecanu, is, according to Pelouze and Liebig, an acid salt. Formula, $2\overline{\mathrm{St}} + \mathrm{GlyO} + 2\mathrm{HO}$. It is the chief ingredient in most kinds of suet or tallow, and is the most important of the fatty bodies.

To obtain pure stearine, mutton suet is melted in the water-bath, mixed with ten parts of ether, and set aside to cool. The crystals which are deposited on cooling are strongly pressed, and washed with cold ether. They are pearly scales, which feel soft, but not greasy; fusible about 140° to 145°; and congealing to a mass like wax, not crystalline, and easily reduced to powder. It is insoluble in water, soluble in hot alcohol and ether; both of which solvents, on cooling, deposit almost the whole of the stearine. When distilled, it yields the products of the action of heat on stearic acid, which are margaric acid and margarone, besides a carbo-hydrogen, as well as the products of the distillation of glycerine, particularly acroleine.

Stearine has weak acid properties. By careful management it may be made to combine with potash, forming a compound from which acids separate stearine, and not stearic acid. The probable formula of this compound is $2\overline{\mathrm{St}} + \mathrm{GlyO} + \left.\begin{matrix}\mathrm{KO}\\ \mathrm{HO}\end{matrix}\right\}$.

But when stearine is boiled with caustic alkalies, stearate of potash is formed, while hydrated oxide of glycerule (glycerine) is separated. From 100 parts of stearine, Chevreul obtained 102·6 parts of hydrated stearic acid and glycerine together; the glycerine weighed 8 parts. If we admit that 3 at. of water are taken up in this process, two by the half of the stearic acid, and one by the glycerine, 100 parts of stearine should yield, according to the formula of Pelouze and Liebig, 102·3 parts of stearic acid and glycerine; the latter weighing 7·9 parts. This close correspondence not only lends additional probability to the formula given above, but is a wonderful proof of the accuracy of Chevreul in his splendid researches on fatty bodies, made when nothing was known of these compounds.

According to Pelouze and Boudet, the solid part of the butter of cacao is a compound of the above stearate of oxide of glycerule with the corresponding oleate.

Stearate of Potash.—*a.* Acid. $\overline{\mathrm{St}},\left.\begin{matrix}\mathrm{KO}\\ \mathrm{HO}\end{matrix}\right\}$. (Chevreul.) To prepare it, the solution of 1 part of the neutral stearate is diluted with 1000 parts of water, when the acid salt separates. It is purified by washing with water and solution in alcohol, from which it crystallizes in pearly scales. One thousand parts of boiling water form with 1 of this salt a milky solution, which contains neutral stearate dissolved; while the suspended salt is a still more acid compound, $2\overline{\mathrm{St}},\mathrm{KO},3\mathrm{HO}$. Three atoms of acid stearate, $3(\overline{\mathrm{St}},\mathrm{KO},\mathrm{HO})$, produce 1 atom of neutral salt, $\overline{\mathrm{St}},2\mathrm{KO}$; and 1 at. of the new salt, $2\overline{\mathrm{St}},\left.\begin{matrix}\mathrm{KO}\\ 3\mathrm{HO}\end{matrix}\right\}$. The latter is fusible into an oily liquid, while the original acid salt is only softened by heat. (Chevreul.)

b. Neutral. $\overline{\mathrm{St}},2\mathrm{KO}$. When equal weights of stearic acid and potash are dissolved in 10 parts of hot water, the neutral salt separates on cooling in opaque grains, which are to be squeezed and purified by solution in hot alcohol, from which it crystallizes in shining scales and needles. With 10 parts of cold water, this salt forms an opaque viscid solution. It is soluble in 25 parts of hot water; more soluble in solution of potash. From this latter solution, when hot and saturated, the addition of chloride of potassium separates the salt entirely in the form of an opaque viscid mass, which, on cooling, forms a firm soap. If chloride of sodium be employed, the salt which separates is neutral stearate of soda, which on cooling forms a very hard soap.

Neutral stearate of potash, as above described, is resolved by 1000 to 5000 parts of cold water into potash, which remains dissolved, and acid stearate, which separates. (Chevreul.) The neutral salt is soluble in hot alcohol, and on cooling forms a jelly (opodeldoc). It is insoluble in ether.

Stearates of Soda.—*a.* Acid. $\overline{\mathrm{St}},\mathrm{NaO},\mathrm{HO}$. Prepared from the neutral salt like the corresponding salt of potash, which it resembles.—*b.* Neutral. It is prepared like the neutral soap of potash from 20 parts of stearic acid, 13 of soda, and 300 of water. It may be obtained either in crystals from alcohol, or as a hard soap from water by adding chloride of sodium to the hot saturated aqueous solution, an excess of soda being also present. The action of water and alcohol on this soap is much the same as on the neutral salt of potash, only the soda soap is less soluble and less easily decomposed by water, requiring at least 2000 parts.

The *Stearates* of Baryta, Strontia, and Lime, are all neutral, according to the general formula, $\overline{St},2MO$. They are white insoluble precipitates.

Neutral Stearate of Lead, $\overline{St},2PbO$, resembles the preceding.

Basic Stearate of Lead, $\overline{St},4PbO$, prepared by boiling stearic acid with subacetate of lead, is a transparent soap or plaster fusible at 212°.

Acid Stearate of Lead is formed by melting 100 parts of stearic acid with 21 of oxide of lead. It is also a transparent soap or plaster, fusible at 212°.

ON THE COMPOSITION OF STEARIC AND MARGARIC ACIDS.

As already mentioned, the recent researches of Varrentrapp, Redtenbacher, Bromeis, and Stenhouse, lead to the following formulæ for the two hydrated acids:

Hydrated margaric acid, $C_{68}H_{68}O_8$ or $C_{34}H_{34}O_4$.
Hydrated stearic acid, $C_{68}H_{68}O_7$.

Margaric acid forms with oxide of silver a salt, the formula of which is $C_{34}H_{33}O_3,AgO$, so that the hydrate might be supposed to be $C_{34}H_{33}O_3,HO$; but as it forms two series of salts, in one of which only half this quantity of water is replaced by a base, we are induced to consider it a bibasic acid, $C_{68}H_{66}O_6,2HO$. The margarate of silver will then be $C_{68}H_{66}O_6,2AgO$. Taking this view, and comparing it with stearic acid, we find it to contain 1 atom of oxygen more than that acid, while the carbon and hydrogen remain exactly in the same proportion. If we now call this compound of carbon and hydrogen margarule $= C_{34}H_{33} = Ml$, we find that anhydrous margaric acid $= 2(MlO_3)$ and anhydrous stearic acid $= Ml_2O_5$. Again, comparing 1 atom $= \frac{1}{2}$ equivalent of margaric acid, $= MlO_3$, with 1 equivalent of stearic acid, we find them to bear the same relation to each other as sulphuric and hyposulphuric acids, SO_3 and S_2O_5. The only difference is, that while sulphuric acid is monobasic as well as hyposulphuric acid, the two acids of margarule, which may be called margarulic and hypomargarulic acids, are both bibasic.

If this be really the relation between margaric and stearic acids, if they be different oxides of the same radical, we should expect to be able to convert stearic (hypomargarulic) acid into margarulic acid by oxidising agents. This is in fact the case, as formerly described. The change is effected by the action not only of nitric acid, but of a mixture of sulphuric acid and bichromate of potash. Moreover, just as hyposulphuric acid, S_2O_5, is resolved by heat into sulphurous acid, SO_2, and sulphuric acid, SO_3, so hypomargarulic (stearic) acid, when distilled, is resolved into oxide of margarule (margarone), MlO, and margarulic acid, MlO_3; that is, in both cases, one portion yields oxygen to another; thus,

$$S_2O_5=SO_3+SO_2 \text{ and } 2Ml_2O_5=3MlO_3+MlO.$$

All these facts render it almost certain that the above is a true account of the constitution of margaric and stearic acids.

The original analyses of Chevreul, indeed, gave for anhydrous margaric acid the formula $C_{70}H_{65}O_3$, or the half of this $=\frac{C_{70}H_{65}O_3}{2}$; and for anhydrous stearic acid the formula $C_{70}H_{67}O_5$. But not only was the method then used for determining the atomic weights of the acids inferior to that now employed, but the acids themselves were possibly not absolutely pure. It is worthy of remark, however, that Berzelius, observing that in these acids, according to Chevreul, the same quantity of carbon, 70 atoms, was combined with 3 and 5 atoms of oxygen, was the first to suggest that they were most probably oxides of the same carbo-hydrogen. This suggestion appears now to be established, and is only another instance of the profound sagacity of Berzelius.

It should also be mentioned here, that five careful analyses of stearine (acid stearate of oxide of glycerule), by Pelouze and Liebig, gave the following results:

Carbon . .	75·981	to	76·600	per cent.
Hydrogen .	12·240	to	12·170	per cent.
Oxygen . .	21·779	to	21·330	per cent.

Adopting for stearic acid the formula of Chevreul, and for oxide of glycerule that of Pelouze, these numbers correspond to the formula $2\bar{S}t$,GlyO,2HO, which has been given above. But if we take for stearic acid the formula of Redtenbacher, and for oxide of glycerule the formula C_3H_2O, the formula most nearly agreeing with the numbers will be $\overline{St},GlyO,2HO$. The former gives $C_{146}H_{143}O_{17}$, the latter $C_{71}H_{70}O_8$. The former would give

Carbon	76·21	the latter,	Carbon	76·43
Hydrogen	12·18	,,	Hydrogen	12·30

Both are obviously near the truth; but, as long as there is any doubt as to the composition of oxide of glycerule, that of stearine cannot be satisfactorily determined. Notwithstanding the improvements which have been introduced into organic analysis, and the progress which has been made in the study of these substances, the results obtained by Chevreul in his masterly researches have undergone but little modification, except in the interpretation of the analytical part of his immortal work; the numerical results being correct in a degree quite wonderful, when we consider the difficulties then attending organic analysis; and, above all, that the whole subject of the fatty bodies was then untouched, insomuch that, till Chevreul discovered them, the oily acids were unknown, and the nature of soaps altogether misunderstood.

ACTION OF HEAT ON STEARIC AND MARGARIC ACIDS.

When these acids are distilled, they yield a product, the melting point of which is almost the same as that of the acids; and hence they were formerly supposed to distil nearly unchanged, although Chevreul had observed that the product was no longer entirely soluble in alkalies.

Redtenbacher and Varrentrapp have lately examined this subject minutely, with the following results.

Pure stearic acid, melting at 158°, yields a solid product, which melts at about 156°. This is a mixture of pure margaric acid, melting at 140°, and a neutral crystalline fat melting at 190°, besides a liquid substance. This mixture is dissolved by potash, forming a milky liquid, which is precipitated by chloride of calcium. The precipitate, boiled with ether, leaves pure margarate of lime; while the ether being evaporated leaves the solid and liquid neutral compounds above mentioned. The former is margarone; the latter a carbo-hydrogen.

When stearic acid is distilled with one quarter its weight of quicklime, carbonate of lime is left in the retort, while margarone and the carbo-hydrogen distil over.

It is particularly to be observed, that the products of the distillation of stearic and margaric acids contain no substance soluble in water, and particularly no *sebacic acid.*

Margarone.—Discovered by Bussy. Obtained by distilling stearic or margaric acids with or without lime. It is purified by crystallization from ether.

Margarone is a white, crystalline, friable fat, fusible generally at 190°, but sometimes at 200° and upwards; indicating the existence of more than one compound, the composition of which, however, seems to be nearly uniform. The analyses of margarone by Bussy, Redtenbacher, and Varrentrapp indicate two formulæ, between which it is difficult to decide. The first is $C_{33}H_{33}O$, which may arise from anhydrous margaric acid by the loss of 1 at. carbonic acid; $C_{34}H_{33}O_3 - CO_2 = C_{33}H_{33}O$. This would account for the agency of lime in its production. Again,

$$\begin{array}{l}
\text{4 at. hydrated stearic acid} \quad . \quad = C_{272}H_{272}O_{28} \text{ might yield} \\
\left.\begin{array}{ll}
\text{6 at.=3 eq. hydrated margaric acid} & C_{204}H_{204}O_{24} \\
\text{1 at. water} \quad . \quad . \quad . & \phantom{C_{33}}\,H\;\;O \\
\text{1 at. margarone} \quad . \quad . \quad . & C_{33}\,H_{33}\,O \\
\text{1 at. carbonic acid} \quad . \quad . & C\qquad\;\; O_2 \\
\text{1 at. carbo-hydrogen} \quad . \quad . & C_{34}\,H_{34}
\end{array}\right\} = C_{272}H_{272}O_{28}
\end{array}$$

On the other hand, if we adopt for margarone the formula $C_{34}H_{33}O = MlO$, then

$$\begin{array}{ll}
\text{2 at. hydrated stearic acid} & = Ml_4O_{10} + 4HO \text{ yield} \\
\text{3 at. hydrated margaric acid} & = Ml_3O_9 + 3HO \\
\text{1 at. margarone} \quad . & = Ml\,O \\
\text{1 at. water} \quad . \quad . & = \qquad\quad HO \\
\hline
 & Ml_4O_{10} + 4HO.
\end{array}$$

From the margarone the carbo-hydrogen may be formed along with carbonic acid and carbon; for 2 at. margarone $= C_{68}H_{66}O_2 = C_{66}H_{66} + CO_2 + C$. That this does happen is indicated by the deposition of carbon. The formation of margarone from margaric acid and lime is also easily explained.

$$\begin{array}{lll}
\text{2 at. anhydrous margaric acid} & = C_{68}H_{66}O_6 + \text{2 at. lime, 2CaO, yield} & \\
\text{1 at. margarone} = MlO & = C_{34}H_{33}O & \\
\text{2 at. carbonate of lime} & = C_2 \qquad O_4 + & 2CaO \\
\text{1 at. of water} & = \quad HO & \\
\text{Polymeric carbo-hydrogen} & = C_{32}H_{32} & \\
\hline
 & C_{68}H_{66}O_6 + & 2CaO
\end{array}$$

From stearic acid with lime Redtenbacher obtained a compound like margarone, but composed of $C_{46}H_{45}O$. This may be a compound of oxide of margarule with a carbo-hydrogen, $C_{34}H_{33}O + C_{12}H_{12} = C_{46}H_{45}O$.

A similar compound, discovered by Bussy, and called by him stearone, is $C_{68}H_{66}O$. It is possibly Ml_2O, a sub-oxide of margarule.

In all these researches the carbo-hydrogens were found to contain equal equivalents of hydrogen and carbon; but, as they form no combinations from which their atomic weights can be deduced, it is impossible to say whether they may contain one equivalent of each element, or a certain number of CH in one atom. In fact, there appears to be an unlimited number of such carbo-hydrogens, agreeing in relative proportions, but differing in the absolute quantity of their elements; in other words, in their atomic weight.

PRODUCTS OF THE ACTION OF NITRIC ACID ON STEARIC AND MARGARIC ACIDS.

If stearic acid be heated with an equal weight of nitric acid, sp. g. 1·285, for a few minutes, it is entirely converted into margaric acid, while the nitric acid contains no foreign substance. But if the action be continued, the nitric acid being occasionally renewed, the margaric acid is by degrees entirely decomposed, and the liquid on cooling deposits nothing. If evaporated to one half, it deposits *suberic acid;* and contains succinic acid, and an oily liquid soluble in nitric acid. (Bromeis.)

Suberic Acid.—Formula of the anhydrous acid, $C_8H_6O_3$. Symb. $\overline{Su}$. Formula of the crystallized acid, $C_8H_6O_3,HO$. Symb. $\overline{Su},HO$. Discovered by Brugnatelli as the product of the oxidation of cork by nitric acid; by Laurent as a product of the action of nitric acid on oleic acid and olive oil; and by Bromeis as a product of the action of nitric acid on stearic and margaric acids.

The solution of margaric acid in nitric acid after long boiling is evaporated to one half, when it deposits a quantity of crystals. These are washed with cold water, and purified by crystallization. They are hydrated suberic acid. From cork it is obtained by a similar process. It forms a white crystalline powder; fusible, if moist, at 130°, and if dry, at 238°. In a higher temperature it sublimes, condensing into an oily liquid, which congeals into long needles. It is easily soluble in hot water, alcohol, and ether.

In the salts of suberic acid, 1 atom of basic water is replaced by 1 at. of base. Suberate of oxide of ethule is an oily, fragrant liquid, $\overline{Su},AeO$. The alkaline suberates are soluble. Those of baryta, strontia, lime, and silver, are neutral and insoluble. With oxide of lead suberic acid forms a neutral salt, $\overline{Su},PbO$; and a basic salt, $\overline{Su},3PbO$. (Bromeis.)

When suberate of lime, baryta, or strontia is distilled with excess of base, there is obtained, among other products, a liquid boiling at 367°, which absorbs oxygen from the air, or from nitric acid, and is converted into suberic acid. According to Boussingault, its formula is C_8H_7O. It may be considered as a hyduret of suberule, $C_8H_6O + H$, analogous to hyduret of benzule. It may also be the oxide of another radical, C_8H_7.

Succinic Acid. — Formula of the anhydrous acid, $C_4H_2O_3$. Symb. $\overline{S}$. Formula of the sublimed acid, $C_8H_5O_7 = 2\overline{S} + HO$. Formula of the hydrated acid, $C_4H_2O_3,HO = \overline{S},HO$.

Succinic acid exists ready formed in amber (succinum), and in the resins of certain coniferæ. (Unverdorben, Lecanu, and Serbat.) It is also one of the products of the oxidation of stearic and margaric acids.

To obtain it, the products of the distillation of amber are filtered through moistened paper, to separate empyreumatic oil; the filtered liquid is evaporated, and the crystals which it deposits are purified by sublimation. To prepare it from the oily acids, the mother liquid of the suberic acid, as above described, is evaporated, and the crystals which separate are purified from suberic acid by cold ether, which dissolves the latter.

Hydrated succinic acid crystallizes in colourless scales or prisms, of sp. g. 1·55, which are entirely volatile. The sublimed acid contains only half the quantity of water, and by repeated sublimation it may be rendered at last anhydrous.

Anhydrous sulphuric acid acts on it, producing a new acid, in which 2 at. of sulphuric acid and 1 of hydrated succinic acid combine, the elements of 1 at. of water becoming basic. Its probable formula is $C_4H_2S_2O_9,HO$.

Succinic acid, contaminated with the empyreumatic oil formed in the distillation, has been, and still is occasionally, used in medicine. The oil is the active ingredient, probably from containing kreosote.

Succinamide.—This substance is formed by the action of aqua ammoniæ on succinate of oxide of ethule. It is a crystalline solid. Formula, $C_4H_2O_2 + NH_2 = \overline{S},Ad$. It differs from succinate of oxide of ammonium by 2 at. of water. (Liebig.)

Bisuccinamide.—When anhydrous succinic acid is heated in dry ammonia, a crystalline volatile body is obtained, which D'Arcet calls Bisuccinamide. Its formula is $C_8H_3O_4 + NH_2 = (C_8H_4O_6 + NH_3) - 2HO = (2\bar{S} + AdH) - 2HO$. When bisuccinamide is dissolved in water, the solution yields crystals, the formula of which is $C_8H_7NO_6 = (C_8H_4O_6 + NH_3)$; that is, anhydrous bisuccinate of ammonia. But it does not appear to be that salt, but rather bisuccinamide with 2 at. water (of crystallization ?) (D'Arcet).

Some uncertainty exists in regard to the true constitution of succinic acid and its salts. According to the prevailing view, the salts of succinic acid have the general formula, $C_4H_2O_3 + MO$. But Fehling, by recent researches, has rendered it probable that succinic acid is a tribasic acid, and that the hydrated acid is $C_8H_3O_5 + 3HO$. According to this chemist, the following is a view of the succinates.

$$
\begin{array}{ll}
C_8H_3O_5 + AdH_2O & = \text{crystallized succinamide. (Bisuccinamide.)} \\
C_8H_3O_5 + 3PbO & = \text{tribasic salt of lead.} \\
C_8H_3O_5 + \left.\begin{matrix} 2PbO \\ HO \end{matrix}\right\} & = \text{bibasic salt of lead.} \\
C_8H_3O_5 + \left.\begin{matrix} 2AdH_2O \\ HO \end{matrix}\right\} & = \text{bibasic salt of ammonia.} \\
C_8H_3O_5 + \left.\begin{matrix} 2AgO \\ HO \end{matrix}\right\} & = \text{bibasic salt of silver.}
\end{array}
$$

All the succinates are decomposed by distillation.

Succinate of Ammonia.—The solution of the neutral salt is used in analysis to precipitate peroxide of iron. It deposits crystals, which are permanent in the air, and volatile, while the liquid becomes acid. An impure solution was formerly used in medicine.

Succinate of Oxide of Ethule is an oily liquid, of sp. g. 1·036 in the liquid state, and 6·06 in the state of vapour. It boils at 417°. With aqua ammoniæ it forms a crystalline substance, apparently analogous to oxamethane (D'Arcet). The remaining succinates are of little importance. Those of lead and silver are white and insoluble.

Succinone.—When succinic acid is distilled with lime, an oily liquid is obtained, to which D'Arcet has given the name of Succinone. As his analyses of it do not agree together, its formula must be considered unknown.

APPENDIX TO SUCCINIC ACID.

AMBER.

The origin of this well-known substance is still doubtful. It is commonly viewed as having been originally a vegetable balsam or resin, altered by time. But the production of succinic acid from oily acids renders it probable that amber is a product of the decay of wax, or of some other substance allied to the fats or fixed oils.

It is found on the coast of Prussia partly in beds of fossil wood or brown coal, partly on the shore, and at the bottom of the sea. After storms it is found on the shore among the sea-weeds torn up by the agitation of the water. To judge by the remains of vegetables which accompany it, it is the produce of extinct coniferæ, and it frequently contains insects almost always of extinct species. One species is said to exist at the present day in America, and species allied to others occur in Brazil and New Holland. Amber occurs sparingly in other parts of Europe, as in the neighbourhood of London and Paris, Sweden, Poland, Italy, Spain; and also in Siberia and North America; but generally in beds of fossil wood, brown coal, or coal.

Amber occurs in fragments of various sizes. It is transparent or translucent, hard, brittle, of a paler or darker yellow or brown colour, of sp. g. 1·065 to 1·07; tasteless and inodorous, but acquiring an aromatic smell when heated. It becomes highly electric by rubbing, and was the first substance in which this property was observed; hence the term electricity (from ηλεϰτϱον, amber). It melts at about 550°, but is partially decomposed at that temperature. It is insoluble in water, partially soluble in alcohol.

Amber, according to Berzelius, contains succinic acid, a volatile oil, two resins soluble in alcohol and ether, and a bituminous mass insoluble in all menstrua. This last constitutes more than four-fifths of the amber. According to Hünefeldt, hydrochloric acid extracts from amber, besides succinic acid, another acid, very similar to mellitic acid. When amber is distilled, it yields succinic acid, and a volatile oil (oil of amber); while the bituminous residue, dissolved in a mixture of linseed oil and oil of turpentine, forms amber varnish. According to Vogel, a yellowish substance is found along with the acid and oil, which he calls camphor of amber.

The oil of amber is a mobile liquid, of a penetrating smell. It is an ingredient of Eau de Luce, along with alcohol and ammonia, and is used as a stimulating essence in cases of fainting. This oil, when acted on by nitric acid, yields an orange-coloured resinous mass, with a strong musky smell (artificial musk).

OLEIC ACID.

Formula of the acid in the salt of baryta, $C_{44}H_{39}O_4$? Formula of the hydrated acid, $C_{44}H_{39}O_4,HO$? (Varrentrapp.)

According to the analysis of Chevreul, oleic acid is a bibasic acid, and the formula of the hydrate is $C_{70}H_{58\frac{1}{2}}O_5,2HO$. According to Laurent, it is $C_{70}H_{64}O_5,2HO$. But the absolute purity of the acid analysed by Chevreul is doubtful, and that analysed by Laurent had been distilled, in which circumstances it is decomposed. There is reason, however, to believe that there is more than one liquid oily acid, to which the name of oleic acid has been given. The oleic acid of Varrentrapp was obtained from oil of almonds, and from the fluid portion of ox fat. The acid of Chevreul was obtained from the fluid portion of mutton suet.

Oleic acid, combined with oxide of glycerule, is the principal ingredient of the fixed oils, excepting the drying oils. It occurs in smaller quantity in animal fats, probably in large quantity in liquid animal oils; also in bile along with stearic acid; and in the seeds of cocculus indicus.

To obtain oleic acid, almond oil must be preferred, as containing more of it than olive oil, or the fluid portion of animal fats. The drying oils, according to Redtenbacher, contain a distinct acid.

Oil of almonds is saponified, and the soap decomposed by an acid. The resulting oily acid is digested in the water-bath for several hours with half its weight of oxide of lead. The mixture is then agitated with twice its volume of ether, and left for twenty-four hours. The ether dissolves acid oleate of lead, leaving undissolved margarate of lead. The clear ethereal solution is now mixed with diluted hydrochloric acid, when the oleic acid is separated, and rises to the surface dissolved in ether. The ether is removed by gentle evaporation, and the oleic acid again saponified by soda. The soap is now purified by being repeatedly dissolved in solution of soda, and separated by the addition of common salt, by which means it may be rendered colourless, or nearly so. The purified soap yields oleic acid hardly coloured, which is washed with water to remove free mineral acid, and deprived of water by the heat of the water-bath.

Oleic acid thus prepared is an oily liquid, having a slight smell and a pungent taste. It is decidedly acid to test paper, lighter than water, and crystallizes in needles when cooled some degrees below 32°. It is insoluble in water, soluble in alcohol and ether, miscible with oils and fats.

It is decomposed by heat, yielding sebacic acid and other products. Nitric acid converts it into suberic acid and several other acid products; but does not produce any oxalic acid. By nitrate of mercury, or nitrous acid, it is converted into elaidic acid. Of all the oily acids, it is the most easily decomposed.

SALTS OF OLEIC ACID.

Oleic acid decomposes the alkaline carbonates, forming with potash and soda soft soaps. The formulæ of the oleates are not yet determined with certainty.

Oleate of Ammonia.—A gelatinous mass, soluble in cold water.

Oleate of Oxide of Ethule.—A colourless, tasteless, inodorous, oily liquid, of sp. g. 0·871, volatile, easily decomposed by an alcoholic solution of potash. In contact with nitrate of mercury, it is converted into elaidate of oxide of ethule. (Laurent.) It may be distilled with little change. Probable formula, $C_{44}H_{39}O_4,AeO$.

Oleate of Oxide of Methule.—Analogous to the preceding.

Oleate of Oxide of Glycerule.—Syn. Oleine. Unknown in a state of perfect purity. It is an ingredient in almost all oils and fats, in which it is mixed or combined with stearate or margarate of oxide of glycerule, or both. When these oils are subjected to pressure at a low temperature, the more fluid portion is impure oleine, generally containing in solution some compound of oleine with stearine or margarine.

According to Kerwyk, a tolerably pure oleine may be obtained from olive oil, by agitating 2 parts of the oil with 1 of a strong solution of caustic soda, and then adding weak alcohol, when the unsaponified portion rises to the surface. It is washed with weak alcohol, and dried by fragments of chloride of calcium. When animal fat is boiled with alcohol, the hot liquid deposits on cooling stearine and margarine, retaining oleine in solution; and, by repeating this process, it may be got nearly pure.

According to Pelouze and Boudet, the fluid part of fat oils contains two compounds; and the oleine of drying oils is distinguished by the action of nitrous acid. This acid converts the oleine of fat (not drying) oils into a solid mass—elaidate of oxide of glycerule, or elaidine; while it has no apparent action on the oleine of drying oils.

The physical properties of oleine are similar to those of almond oil. Its sp. g. is 0·90 to 0·92. It is converted by alkalies into soap, with the separation of glycerine. By the action of heat or of nitric acid it is converted into the same products as oleic acid, with the addition of the products yielded by glycerine. It absorbs oxygen from the air, and becomes thick. It congeals when exposed to a very low temperature.

Oleate of Potash.—a. Neutral. This compound is formed by heating equal weights of oleic acid and potash with 5 parts of water. It separates from the liquid as a soft mass, which is purified by solution in alcohol, and evaporation to dryness. It forms a white, dry, friable mass, of a bitter alkaline taste. It forms with 2 parts of water a jelly; and dissolves in 4 parts of water, forming a viscid, soapy solution. When the soap made from mutton suet is treated with water, as described under stearic and margaric acids, whereby acid stearate and margarate of potash are precipitated, and when the process has been repeated till water causes no further turbidity, the filtered liquid contains oleate of potash or soda nearly pure. From the salt thus made, the oleic acid of Chevreul was prepared. The solution of oleate of potash precipitates most of the earthy and metallic salts.

b. Acid. This salt is formed by heating 100 parts of oleic acid, about 9 of potash, and 400 of water together. It forms a jelly, insoluble in water, but soluble in alcohol.

Oleate of Soda.—The neutral salt is formed like that of potash, which it much resembles.

The *oleates* of the earths and metallic oxides are insoluble in water, fusible when heated, and soluble in alcohol.

Oleate of Lead is obtained pure by precipitating acetate of lead with impure oleate of potash or soda, made from almond or olive oil, and digesting the precipitate with its own weight of ether, which leaves undissolved margarate and stearate of lead. The oleate of lead softens by the heat of the hand, and has all the properties of a plaster. Oleic acid forms with oxide of lead, besides this neutral oleate, an acid and a basic salt, which are also plasters.

ON THE COMPOSITION OF OLEIC ACID.

It has already been mentioned, that Chevreul obtained from the oleic acid of mutton suet, a different formula from that adopted by Varrentrapp in his recent researches for the oleic acid of oil of almonds and of ox tallow. The differences in their results are so considerable, as to render it probable that they examined different acids. For example, Chevreul found in the oleate of baryta 22·97 p. c. of baryta; while the salt of baryta analysed by Varrentrapp contained only 18·38 p. c. But there is reason to doubt the perfect accuracy of Chevreul's formula, even supposing the acids to be different, from the occurrence in it of a half equivalent of hydrogen.

There can be little doubt of the accuracy of Varrentrapp's formula for the acid analysed by him; for not only was the acid quite free from stearic and margaric acids, but in ten analyses he obtained numbers closely agreeing with his formula; and these analyses were made on oleic acid from different preparations, both as first obtained, and after its saponification or combination with bases, and subsequent separation. Moreover, the analysis of the oleate of oxide of ethule agrees closely with Varrentrapp's formula, $C_{44}H_{39}O_{4},AeO$; and the same remark applies to the analysis of the oleates of baryta and silver.

Further experiments are still required to complete our knowledge of the true constitution of oleic acid.

ACTION OF HEAT ON OLEIC ACID.

When oleic acid is heated, it boils at a high temperature, and is thereby decomposed, yielding solid, liquid, and gaseous products. The gaseous products are carbonic acid and carburetted hydrogen. The liquid portion contains a little undecomposed oleic acid, with several liquid carbo-hydrogens, the boiling point of which varies from 320° to 526°. The solid product, which is most abundant in the first stage of the distillation, is a new acid discovered by Thénard, and called by him Sebacic Acid. This acid is a characteristic product of the distillation of oleic acid from every source, including that from drying oils, and of all fats containing a liquid acid.

SEBACIC ACID.

Formula of the anhydrous acid, $C_{10}H_8O_3$. Formula of the hydrated acid, $C_{10}H_8O_3,HO=\overline{\mathrm{Sb}},HO$. (Dumas. Redtenbacher.)

To obtain it, the whole liquid and solid products of the distillation of oleic acid, oleine, oils, or fats, are boiled with water as long as that liquid deposits anything on cooling. The crystals are washed with cold water, and crystallized from hot water till they become colourless, and free from empyreumatic smell.

Hydrated sebacic acid forms light, white, pearly scales, very like benzoic acid. They melt at 260° to an oily liquid; and at a higher temperature sublime unchanged. It is sparingly soluble in cold water; very soluble in hot water, alcohol, and ether.

SALTS OF SEBACIC ACID.

The cold aqueous solution of sebacic acid causes a white precipitate in the salts of lead or silver. The general formula of the sebates is $\overline{\mathrm{Sb}},MO$.

The *Sebates of Potash, Soda, and Ammonia*, are very soluble and crystallizable. Their solutions precipitate the salts of lime, forming sebate of lime. $\overline{\mathrm{Sb}},CaO$. (Redtenbacher.)

Sebate of Silver, $\overline{\mathrm{Sb}},AgO$, is a white, curdy precipitate, which, when heated, leaves 51·64 p. c. of metal, and yields a sublimate resembling sebacic acid.

Sebate of Oxide of Ethule. $\overline{\mathrm{Sb}},AeO$. Prepared like the ethers of the oily acids generally, by passing hydrochloric acid gas through a solution of the acid in alcohol, and adding water, which separates the new compound. A mobile oily liquid, having a fragrant smell of melons; crystallizable at 16°, and volatile at a temperature above 212°.

The presence of sebacic acid among the products of the distillation of any oil or fatty substance may be considered as positive proof of the presence in that oil or fat of oleic acid, or of a liquid acid closely analogous. Even the drying oils, although the oleic acid they contain appears to be distinct, yield sebacic acid when distilled; while, on the other hand, those oily acids which are solid at ordinary temperatures, such as stearic, margaric, or sericic acids, do not yield the smallest trace of sebacic acid. To ascertain, then, whether an oil, a fat, or an oily acid, contains oleic acid under any of its forms, distil a small portion of it, and boil the product with water. If the filtered liquid deposit crystals on cooling, then oleic acid has been present in considerable quantity. If, again, the liquid deposit nothing, but has acquired the property of precipitating the salts of lead, oleic acid has been present in smaller quantity. But if the water have dissolved nothing, no oleic acid has been present. This is a test of great delicacy, for which we are indebted to Liebig and Redtenbacher.

ACTION OF NITROUS AND NITRIC ACIDS ON OLEIC ACID.

1. *Action of Nitrate of Mercury, or of Nitrous Acid.*

By the action of nitrate of mercury, and more especially by that of nitrous acid, oleic acid is converted into a new acid, solid at ordinary temperatures, to which the name of Elaidic Acid has been given. (Poutet. Boudet. See below, *Action of Nitric and Nitrous Acid on Oils.*)

Elaidic Acid.—To prepare it, a current of nitrous acid, as disengaged from a mixture of starch and nitric acid by heat, is passed for four or five minutes through pure oleic acid at a low temperature. After a short time the liquid congeals into a crystalline mass. This is washed with hot water to remove nitric acid, and then dissolved in its own volume of hot alcohol. On standing, this solution forms a semi-solid mass of crystals, which are purified by pressure and recrystallization. (Meyer.)

Hydrated elaidic acid, thus prepared, resembles sublimed benzoic acid. It melts at 113°; is extremely soluble in alcohol, less so in ether, insoluble in water. When distilled, a great part passes over unchanged; but the product, when boiled with water, yields a solution which precipitates the salts of lead and silver, but deposits no crystals. (Meyer.)

SALTS OF ELAIDIC ACID.

Elaidic acid decomposes the alkaline carbonates, forming salts which, with 6 to 8 parts of water, yield strong soapy solutions.

Neutral Elaidate of Soda is soluble in alcohol, and crystallizes like the acid. Its solution in water when diluted, deposits an acid salt, like stearate and margarate of soda.

Elaidate of Silver is a white curdy soap, which may be obtained in crystals from its solution in aqua ammoniæ.

Elaidates of Lead and Baryta are both white and insoluble.

Elaidate of Oxide of Ethule, prepared by the same process as the other fatty ethers, is an oily liquid, which is decomposed by alkalies. (Laurent. Meyer.)

Elaidate of Oxide of Glycerule.—Syn. Elaidine. This is the compound produced when oleine (oleate of oxide of glycerule) is acted on by nitrous acid or nitrate of mercury. (See *Action of Nitrous Acid on Oils and Fats.*)

ON THE COMPOSITION OF ELAIDIC ACID.

The production of elaidic acid from oleic acid is still unexplained, as it is accompanied by other products not yet sufficiently studied. Among these is a dark red viscid oil, soluble in potash with a blood-red colour, but not forming a soapy solution. (Meyer.)

Laurent observed that oleate of oxide of ethule was changed by nitrate of mercury into elaidate of oxide of ethule, and attributed the change to a simple absorption of oxygen from the nitric or nitrous acid. According to that chemist, oleic and elaidic acids are oxides of the same radical. Thus,

Hydrated oleic acid . = $C_{70}H_{66}O_5,2HO$.
Hydrated elaidic acid = $C_{70}H_{66}O_6,2HO$.

But, however simple this explanation appears, it cannot at present be adopted. Neither of the acids analysed by Laurent was pure; for his elaidic acid melted at 108°, instead of 113°; and his oleic acid had been distilled, which, as formerly mentioned, cannot be done without decomposition. Moreover, his explanation does not include the red oil above-mentioned, or any other product.

Meyer obtained in his recent analysis of elaidic acid, prepared from perfectly pure oleic acid, results indicating the following formulæ :

Anhydrous elaidic acid, $C_{72}H_{66}O_5$.
Hydrated elaidic acid . $C_{72}H_{66}O_5$,2HO.

And the analysis of the elaidates of silver and of oxide of ethule agreed closely with these numbers. Boudet's analysis of the salt of silver, made with an acid which melted at 113°, like Meyer's, had given the same result. Meyer has also shown, that when oleic ether is converted into elaidic ether, the same reddish oil is produced as when oleic is converted into elaidic acid.

If from 2 at. of oleic acid, according to the analysis of Varrentrapp $= C_{88}H_{80}O_{10}$, we subtract 1 at. of elaidic acid, hydrated (Meyer) $= \underline{C_{72}H_{68}O_7}$, there remain the following numbers—
$C_{16}H_{12}O_3$; in which we find carbon and hydrogen in the same proportions as in acetule, C_4H_3: so that, by oxidation, acetic acid might be formed along with elaidic acid. This, however, has not been shown to occur.

The yellow or red oil above-mentioned seems to be an essential accompaniment of the production of elaidic acid. It appears to contain deutoxide of nitrogen or nitrous acid; which explains the circumstance that no other oxidising agent, except nitrate of mercury or nitrous acid, can convert oleic into elaidic acid.

2. *Oxidation of Oleic Acid by Nitric Acid.*

The action of colourless nitric acid on oleic acid has been studied by Laurent, who has discovered among the products a series of new acids, of which one alone, namely suberic acid, was previously known to chemists. Bromeis has recently repeated his experiments, and confirmed most of his results. As the experiments of both, however, were made on impure oleic acid, containing margaric, and perhaps stearic acid, it is impossible at present to ascribe the origin of all these new compounds to the oleic acid alone.

In this action, nitric acid of sp. g. 1·42, previously diluted with its volume of water, is employed. If concentrated, the action is almost explosive. Even with the diluted acid it is at first very violent, but afterwards becomes regular and moderate; and with the aid of heat, and a proper supply of nitric acid, the oleic acid is at last entirely dissolved. The vapours of nitric and nitrous acids, which distil over during the process, carry with them a small quantity of an oily fluid, which attacks the organs of respiration, having a most pungent smell.

The solution when completed, and when margaric acid is no longer deposited on cooling, contains the following acids: suberic acid; azelaic acid; pimelic acid; adipic acid; lipic acid; and an oil soluble in nitric acid. Suberic acid is the most abundant product.

The acid solution is evaporated to one-half, and on cooling deposits a mass of crystals, which are placed to drain in a funnel stopped with asbestus, and washed with cold water. They are suberic acid. When dissolved in hot water, there generally separates an oil or fat, soluble in nitric acid, insoluble in water. When purified by crystallization from alcohol, it forms an oily acid, fusible at 86°, and soluble in alkalies with a blood-red colour.

According to Bromeis, the suberic acid thus obtained is pure; but Laurent found it contaminated with azelaic acid, which resembles it in appearance, but may be separated by ether, in which the latter is very soluble. The formula of azelaic acid, according to Laurent, is $C_{10}H_8O_4,HO$; differing from suberic acid by containing 1 at. of oxygen and 1 at. of hydrogen more. But, as it contained suberic acid, this formula is doubtful. The difference in the results of Laurent and Bromeis probably depends on the fact, that the oleic acid of the former contained margaric acid, while that of the latter contained stearic acid.

Pimelic Acid.—Formula, $C_7H_5O_3,HO$. (Laurent. Bromeis.) The liquid which has deposited the suberic acid is further evaporated, and allowed to stand for some time, when it deposits more suberic acid in light soft crystals, and pimelic acid in hard crystalline grains. These are first washed with cold water and cold alcohol, which remove most of the suberic acid, and purified by repeated solution in hot water and crystallization. It melts at 273°, and at a higher temperature sublimes in fine pearly scales.

Pimelate of Silver, $C_7H_5O_3,AgO$, is white and insoluble.

Adipic and Lipic Acids.—The mother liquid of the preceding acids is very gently evaporated, and set aside for some days. Crystals are deposited, and the liquid remaining is treated in the same way as long as it yields any crystals. The crystals are collected and purified by solution in hot water, when some of the oil formerly mentioned separates. On cooling, the solution deposits brownish crystals of adipic and lipic acids. They are dissolved in ether, and the solution allowed to evaporate to one-half. Crystals are formed, and the mother liquid, by further evaporation, yields more. The two portions are separately boiled with alcohol, and there is obtained on the one hand adipic acid in rounded grains, and lipic acid in fine long plates. Both are purified by recrystallization.

Adipic Acid forms round or hemispherical radiated masses, of a brownish colour, very soluble in hot water. It melts at 266°, and may be sublimed unaltered. All its salts, except the adipate of silver, seem to be soluble. According to Laurent, the anhydrous acid is $C_6H_4O_3$; and the hydrate, $C_6H_4O_3,HO$. According to Bromeis, the acid melts at 293°, and its formula is $C_{14}H_9O_7,2HO$; being thus a bibasic acid, derived from 2 at. of pimelic acid, by the replacement of 1 eq. hydrogen by 1 eq. oxygen. The acids analysed by Laurent and Bromeis may really be distinct, although in most properties they agree.

Lipic Acid crystallizes in long plates, and from alcohol the crystals are particularly fine. It is more soluble in water than adipic acid; and resembles oxalic acid, of which latter, however, no trace is formed in the process. It is fusible at 290°, and sublimes without change in crystals. Formula, $C_5H_3O_4,HO$. (Laurent.)

There generally remains more or less of an oily liquid on the surface of the nitric acid, with which oleic acid has been boiled till with an excess of acid no farther action is observed. According to Laurent, if this liquid be boiled with alcohol and sulphuric acid, it yields an ether, which he considers to be a compound of oxide of ethule with another new acid, *azoleic acid.* By decomposing the ether, he obtained the acid as an oily liquid, the formula of which he considers to be $C_{13}H_{13}O_4$. But, as there is no evidence of its purity, its existence and formula as a separate acid are alike doubtful. According to Bromeis, the oily liquid above-mentioned contains several oily acids; one of which, when the oil is digested with alcohol, readily forms an ether, which seems to be butyrate of oxide of ethule.

Laurent states, that when equal weights of oleic acid and nitric acid are heated together, and the residue well washed and treated with alcohol, œnanthic ether is obtained, indicating the formation of œnanthic acid. But, according to Bromeis, the ether thus obtained has not the composition of œnanthic ether; and although its smell is similar, this property may belong to butyric ether, and the ethers of other fatty acids. As butyric and pimelic acids agree in composition, except that the former contains 1 eq. hydrogen more, the occurrence of butyric acid is more probable.

The acid liquid which has deposited the pimelic, adipic, and lipic acids, still contains a very soluble acid, not further examined.

ACTION OF ALKALIES AT A HIGH TEMPERATURE ON OLEIC AND ELAIDIC ACIDS.

When these acids are heated with 3 volumes of strong alkaline ley till the water is dissipated, and the alkali begins to melt, a violent effervescence occurs, owing to the escape of free hydrogen gas. Water is here evidently decomposed, its oxygen uniting with some of the elements of the oily acids. The alkali is found to be united with a new acid, and with acetic acid. If the mass be acted on with a little water, the salt of the new acid separates as a soap.

The oily acid of this soap is separated and purified in the usual way. It crystallizes from alcohol, melts at 143°, and is friable. Oleic and elaidic acids yield the same new acid. According to Varrentrapp, its discoverer, its formula is $C_{32}H_{30}O_3,HO$. This explains its formation: for if from

1 at. oleic acid . . .	$C_{44}H_{39}O_4$	we subtract
1 at. of the new acid .	$C_{32}H_{30}O_3$	
there remain	$C_{12}H_9\ O.$	

Now $C_{12}H_9O + O_8 = 3(C_4H_3O_3)$, that is, 3 at. acetic acid. The 8 at. of oxygen are obtained from water, and 8 at. of hydrogen disengaged. Again, 1 at. of elaidic acid ($C_{72}H_{66}O_5$) + 7 at. of oxygen contain the elements of 2 at. of the new acid, and 2 at. of acetic acid. These are additional proofs of the accuracy of the formulæ of Varrentrapp and Meyer for oleic and elaidic acids.

ACIDS OF CASTOR OIL.

When castor oil is saponified, the soap yields a mixture of two oily acids; one solid at ordinary temperatures, the other liquid.

The former melts at 266°, forms soaps with alkalies, and has been called Margaritic Acid. Formula, $C_{35}H_{31}O_6$? (Bussy and Lecanu. Laurent.)

The latter congeals at 21°. Its properties and composition may be considered unknown.

Castor Oil.—This oil is a mixture of the compounds of oxide of glycerule with the acids last mentioned. One of these oils is a fusible margarine or fat, the other liquid. Both differ from ordinary margarine and oleine.

Castor oil is extracted from the seeds of Ricinus communis. It is, when pure, pale, viscid, and nearly devoid of taste or smell. Its use as a purgative is well known. It is completely soluble in its volume of absolute alcohol, which furnishes the means of detecting its adulteration with other oils. By nitrous acid it is slowly converted into palmine, a substance analogous to elaidine, but differing from it.

APPENDIX TO THE OILY ACIDS. NATURAL FIXED OILS AND FATS.

The term fixed oil, or fat, in general signifies a compound of oxide of glycerule with certain organic acids. Such compounds are exclusively natural products, not one having as yet been formed artificially.

Among animals they occur chiefly in the cellular membrane; among plants in the seeds, capsules, or pulp surrounding the seed; very seldom in the root. They all, when fluid or melted, make a greasy stain on paper, which is permanent. They are decomposed by acids, which combine with or destroy the oxide of glycerule; and by alkalies, which unite with the acids, setting free the oxide of glycerule. The latter process is called saponification, because the compounds of the oily acids with alkalies have the properties of soap.

The most abundant oils and fats are compounds of oxide of glycerule with stearic, margaric, and oleic acids; two of these, and often all three, being present. Indeed, neither stearate, margarate, nor oleate of oxide of glycerule is yet known in a state of purity. From what has been said of these three compounds, which for brevity we shall call stearine, margarine, and oleine, the consistence of the oil or fat depends on the predominance of one or other. Where stearine predominates, the fat is firm and solid; if margarine be most abundant, it is soft, like lard; while, if oleine predominate, it is liquid. It is obvious that a mixture of stearine and oleine in certain proportions will have the consistence of margarine.

Fixed oils and fats are generally inodorous. Where they possess a peculiar smell, this is always owing to the presence of a compound of oxide of glycerule with a volatile oily acid, such as butyric or hircic acid.

Fats are more fusible than the acids they contain; but at low temperatures they are harder. By pressure between warm plates, the greater part of the oleine of fats may be separated. The remaining fat is harder, less fusible, and less greasy, in proportion as it approaches to pure stearine. At low temperatures the oils assume exactly the aspect of fats. The solid parts of fats and oils are sometimes nearly pure stearine or margarine; in other cases they are definite compounds of stearine or margarine with oleine. Such is the case with the solid part of olive oil, and with the butter of Theobroma cacao.

Oils and fats may be divided into two well-marked classes, according to the action of atmospherical air, or of nitrous acid and nitrate of mercury, on them.

The first of these classes contains the drying oils; so called, because, when exposed to the air, they absorb oxygen, and are converted into a transparent, tough, dry mass, or varnish. The drying oils, moreover, are not solidified by nitrous acid or nitrate of mercury.

Of the nature and constitution of the drying oils, but little is known. They may be saponified by alkalies, but the acid of these soaps is different from ordinary oleic acid, and dries in the air, like the oil from which it is obtained. They also contain oxide of glycerule. Many of the drying oils contain stearine or margarine, or both, dissolved.

The second class, which may be called that of the fat oils, contains those oils and fats which do not dry on exposure to air, and which, when liquid at ordinary temperatures, are solidified by nitrous acid or nitrate of mercury.

Owing to the impurities which oils and fats in their natural state contain, such as membrane, mucus, or albumen, and which act like yeast in promoting chemical action, most of them, when kept, become rancid, as it is called. This change is produced by the absorption of oxygen in part; while the oily acids are set free, and sometimes, as in palm oil, oxide of glycerule is liberated. The rancid smell is owing to the production, at the expense of the elements of the oxide of glycerule, the impurities, and the oxygen of the air, of a volatile body which appears to be acid, as alkalies remove it. Pure stearine, margarine, and oleine do not become rancid.

ACTION OF HEAT ON OILS AND FATS.

The action of heat on oils is very remarkable. At a high temperature they boil, giving off carbonic acid with a little inflammable gas, and a substance, *acroleine*, possessed of a most pungent odour, attacking the eyes most painfully. They acquire a darker colour, and on cooling generally assume the consistence of butter or lard. Oils when distilled become more solid, fats less solid.

When the drying oils are heated, they become thick and viscid, and afterwards dry much more rapidly than before. Hence the advantage of boiling oils intended for oil varnish.

When the fixed oils and fats are distilled, they yield, besides carbonic acid and inflammable gas, a crystalline product, principally margaric acid, mixed with sebacic acid, arising from the oleic acid, acroleine, proceeding from the oxide of glycerule, and an oily liquid, insoluble in alkalies, which is commonly a carbo-hydrogen. A portion of oleic acid also distils unchanged. The first half of the product is solid, owing to the predominance of margaric acid; the second half liquid. No stearic acid is found in either; it is converted into margaric acid.

It has already been stated that the sebacic acid arises exclusively from oleic acid, whether from fat or drying oils, with the exception of castor oil, which does not yield it. Stearic and margaric acids, as well as pure stearine and margarine, do not yield a trace of it.

On the other hand, none of the known oily, or fat acids, when distilled alone, yields the smallest trace of acroleine, the substance to which is owing the insupportably pungent smell of distilled oils or fats. We can only, therefore, ascribe the origin of acroleine to the action of heat on oxide of glycerule; and, in point of fact, hydrated oxide of glycerule (glycerine), when distilled alone, yields it in large proportion. Hence the occurrence of acroleine among the products of the distillation of a fat or oil is a sure and delicate test of the presence of glycerine in the oil.

When the products of the distillation of lard or olive oil are collected in a series of well-cooled bottles containing water, the second and third bottles contain the greater part of the very volatile acroleine, partly dissolved in the oily liquid on the surface, partly in the water below. If the water be again distilled, it yields an oil, soluble in water, and having in the highest degree the insupportable smell of acroleine. Acroleine is unknown in a state of purity; and is remarkable for the rapidity with which it absorbs oxygen from the air, becoming acid. Even in close vessels its solution is decomposed, yielding a tasteless, inodorous, and very indifferent white solid, not resembling fat, and insoluble in all menstrua yet tried. No compound of acroleine has yet been formed from which it can be again obtained. This remarkable substance requires an especial study.

Castor oil, so peculiar in other respects, yields also peculiar products when heated. Among the products are acroleine, an oil insoluble in alkalies, and some peculiar fatty acids. When about one-fifth of the oil has been decomposed, the residue in the retort suddenly consolidates into a spungy elastic yellow mass, insoluble in all menstrua except strong alkalies, with which it forms a viscid solution.

The oil, insoluble in alkalies, contains a solid and a liquid compound. The fatty acids obtained are two; one solid and volatile, the other liquid; both as yet little examined. No sebacic acid occurs in this process.

When castor oil is distilled with nitric acid a volatile acid is produced, possessing the formula $C_{14}H_{13}O_3 + aq$. This formula differs from that of the œnanthic acid by 1 at. oxygen.

OIL GAS.

When fixed oils are introduced drop by drop into red-hot vessels, they are almost entirely converted into volatile products. Of these a large portion consists of permanent gases,—carbonic oxide, marsh gas, and olefiant gas,—mixed with the vapours of several very volatile liquids. This mixture is oil gas. Owing to the presence of olefiant gas, and of the vapours above-mentioned, its illuminating power is twice that of the best coal gas, and three and a half times that of ordinary coal gas. But this difference is barely sufficient to cover the increased expense of the oil employed, even when of the coarsest quality. The sp. g. of the best oil gas is 0·900.

When oil gas is strongly compressed, as in the process for rendering it portable, the vapours above-mentioned are liquefied. Faraday, who examined the liquid, discovered in it several compounds of carbon and hydrogen. One of these is pure benzole (see Benzole). Another is liquid at 0° or —1°, but gaseous at 32°. It has the same composition in 100 parts as olefiant gas, but twice the density. Hence its formula is double that of olefiant gas. It has been named quadro-carburetted hydrogen. The mixed liquid appears to contain another volatile substance, which, like the benzole, crystallizes at low temperatures, the exact composition of which is not sufficiently known ; and in the less volatile portion, another liquid, having apparently the composition, in 100 parts, of olefiant gas. The great illuminating power of oil gas is owing to the presence of the vapours of these carbo-hydrogens. For details, the reader is referred to the Memoirs of Faraday in the Philosophical Transactions.

ACTION OF SIMPLE SUBSTANCES ON FIXED OILS.

The action of oxygen has been already mentioned. The fixed oils are decomposed by chlorine and bromine, yielding hydrochloric and hydrobromic acids, along with other products not yet examined. They generally dissolve iodine, forming a brown solution. They also dissolve sulphur and phosphorus, and such solutions are occasionally used in medicine. When strongly heated with sulphur, the oils undergo a change not yet investigated. The mixture thus formed, is called balsam of sulphur. For use it is dissolved in oil of turpentine or oil of aniseed.

ACTION OF ACIDS ON FIXED OILS AND FATS.

1. ACTION OF SULPHURIC ACID.

The oils are decomposed by strong sulphuric acid. If the quantity of acid be small, it combines with the oxide of glycerule, setting free the oily acids. But when more acid is used, very remarkable changes occur, which have been studied by Fremy in the case of olive oil.

When sulphuric acid is gradually added in the cold to twice its volume of olive oil, bisulphate of the oxide of glycerule is formed on the one hand, and on the other compounds of sulphuric acid with margaric and oleic acid. The mixture becomes tough; and, if mixed after twenty-four hours with two volumes of water, the sulphates of the oily acids, being insoluble in the diluted acid, rise to the surface as a syrupy liquid. This mixture, when freed from adhering acid by washing with a little cold water, dissolves in a larger quantity of water. The sulphate of margaric acid has not yet been separated from that of oleic acid; but the solution containing these compounds is decomposed when kept, or when heated, yielding five new acids. (Fremy.)

When the solution is long kept at ordinary temperatures, the sulphuric acid separates; a mixture of two new acids, metamargaric and metoleic acids, rises to the surface; and a third, hydromargaritic acid, remains dissolved in the water along with the sulphuric acid. If the original solution be heated, there rises to the surface a mixture of these three acids, with a fourth, hydroleic acid; and, when this mixture is boiled with alcohol, there is deposited on cooling a fifth acid, hydromargaric acid, which appears to be formed by the mutual action of metamargaric and hydromargaritic acids. (Fremy.)

Metamargaric Acid.—Symb. $\overline{\mathrm{mMr},}\ 3\mathrm{HO}$? The mixture deposited in the cold by the above solution is exposed to strong pressure to separate the metoleic acid, and the residue purified by crystallization from alcohol, in which the latter acid is sparingly soluble. Metamargaric acid is a white solid, fusible about 112°, and crystallizing on cooling. It is insoluble in water, soluble in alcohol and ether.

When heated with oxide of lead, it loses 3 at. of water, which appear to be replaced by 2 at. of oxide,—a very unusual occurrence, if confirmed. Its salts have been little studied; but it seems to form with potash, soda, and ammonia, neutral and acid salts, the former gelatinous, the latter soluble in alcohol and crystallizable.

Hydromargaritic Acid.—Symb. $h\overline{Mt}$, 2aq.? When the solution above-mentioned has ceased to deposit any more metamargaric and metoleic acids, it is boiled, when a mixture of hydromargaritic and hydroleic acids rises to the surface. Cold alcohol removes the latter, and leaves hydromargaritic acid as a white solid, insoluble in water, but soluble in alcohol and ether. It forms colourless prisms, which are friable, and melt at 155°. By heat it is resolved into water and metamargaric acid. Its salts resemble those of the preceding acid, but are as yet little known.

Hydromargaric Acid. — Symb. $\overline{hMr}$,2HO. This acid, as already stated, is formed when the mixture containing the two preceding acids, along with the two remaining ones, is boiled in alcohol. On cooling, the new acid is deposited in crystals. It is best obtained by melting together 1 equivalent of the two preceding acids, and crystallizing the mass from alcohol. It generally crystallizes in large hemispherical masses, is much more soluble than the two acids from which it is formed, and melts at 140°. It forms a series of salts, which, although analogous, are quite distinct from those of the preceding acids. By the action of heat it yields metamargaric acid.

ON THE COMPOSITION OF THE THREE PRECEDING ACIDS.

Fremy, the discoverer of these acids, has proposed a very simple explanation of their formation. Adopting for margaric acid the formula $C_{70}H_{69}O_8$, he considers metamargaric acid to be formed from it by the assimilation of the elements of two at. water; and its formula will be $C_{70}H_{73}O_{12} = C_{70}H_{71}O_{10}$,2HO. But not only is the formula thus adopted for margaric acid irreconcileable with the analyses of Varrentrapp, but the analyses of the new acids by Fremy do not sufficiently support his formulæ. Fremy adopts for hydromargaric acid the formula $C_{70}H_{71}O_{10}$, and considers it as formed from

$$\begin{array}{lll} & \text{1 at. metamargaric acid} & = C_{70}H_{73}O_{12} \\ + & \text{1 at. hydromargaritic acid} & = \underline{C_{70}H_{70}O_{9}} \\ & & \quad C_{140}H_{143}O_{21} \\ - & \text{1 at. of water} \quad . & = \underline{\quad H \quad O} \text{ leaving} \\ & \text{2 at. hydromargaric acid} & = C_{140}H_{142}O_{20} \end{array}$$

But if the preceding formula be erroneous, this cannot be a correct account of its production.

If we consider hydromargaritic acid a bibasic acid, and deduce its composition from its analysis as contained in the salt of silver, we obtain the formula $C_{74}H_{74}O_{10}$; and for the hydrate $C_{74}H_{76}O_{12}$. If now we subtract 2 at. of carbonic acid and 2 at. of water, there remain $C_{72}H_{74}O_{6}$; proportions which agree much more closely with the numerical results of Fremy's analysis of the anhydrous metamargaric acid than the formula which he has adopted, namely, $C_{70}H_{67}O_{6}$; and which, moreover, explain the conversion of hydromargaritic acid into metamargaric acid by the action of heat. With regard to hydromargaric acid, the analysis of Fremy may be better interpreted by the formulæ $C_{73}H_{75}O_{9}$ for the dry, and $C_{73}H_{77}O_{11}$ for the hydrated acid, than by those he has chosen. If we take the formula of the hydrated acid, on this supposition, and double it,

we have . . . . $C_{146}H_{154}O_{22}$, and if we
subtract 1 at. metamargaric acid $= C_{72}\ H_{74}\ O_{6}$
and 1 at. hydromargaritic acid $= \underline{C_{74}\ H_{74}\ O_{10}}$
there remain 6 at. of water . $H_{6}\ O_{6}$; so that

the production of this acid from the other two may be as easily explained as on Fremy's view. Hitherto, however, the atomic weights of these acids, as deduced from their salts, agree with neither of the above views.

The more recent researches of Varrentrapp and Miller have thrown some doubt on the exactness of the numerical results of Fremy, on which both the above views are founded. According to Miller, both hydromargaric and hydromargaritic acids become solid about 35° below the point at which they melt; a fact which excites the suspicion that they may both be mixtures of two distinct compounds.

Berzelius has proposed a third view of the composition of these acids, also founded on the analysis of Fremy. He assumes the existence of a radical, piotine $= C_{35}H_{35}$. Calling this $= R_{2}$, we have

$R_{2}O_{3}$ = metamargaric or piotinous acid.
$R_{2}O_{4}$ = hydromargaric or hypopiotinic acid.
$R_{2}O_{5}$ = hydromargaritic or piotinic acid.

The resulting formulæ, when calculated to 100 parts, agree most exactly with the actual numerical results of Fremy; but not only are these doubtful, but by adopting the formulæ of Berzelius we lose all insight into the formation of these acids from margaric acid, and this is the chief object of the analytical investigation.

To show how little confidence is due to the coincidence of numbers, when unsupported by the study of the nature of the substance, and the products accompanying its formation, it may be stated, that if we choose to consider hydromargaritic acid as the acid margarate of ethule, which it certainly is not, the formula $\overline{\mathrm{Mr}},\mathrm{AeO},3\mathrm{HO} = C_{74}H_{75}O_{12}$, when reduced to 100 parts, gives numbers exactly corresponding to Fremy's analysis of the acid.

METOLEIC AND HYDROLEIC ACIDS.

These acids arise from the action of sulphuric acid on oleic acid, as the three former do from margaric acid.

Metoleic Acid.—Symb. $\overline{\mathrm{mOl}},2\mathrm{HO}$. When metamargaric acid is prepared as before described, this acid remains undissolved by the alcohol. It is purified by repeated boiling with alcohol and by exposure to cold, when the metamargaric acid crystallizes out. It is a liquid, insoluble in water, very soluble in ether, and by heat converted into carbonic acid and a carbo-hydrogen. It is distinguished from oleic and hydroleic acid by its sparing solubility in alcohol. According to Fremy, in its salts 1 at. of water is replaced by 2 at. of base, which is very unlikely.

Hydroleic Acid. — Symb. $\overline{\mathrm{hOl}},2\mathrm{HO}$. In the preparation of hydromargaritic acid, hydroleic acid is removed by cold alcohol, in which it is extremely soluble, and by which it may be purified. It forms a liquid, insoluble in water, very soluble in alcohol and ether. Heated with oxide of lead it loses 2 at. of water, which are replaced by 2 at. of oxide. In its other salts, according to Fremy, 2 at. of base only displace 1 at. of water.

When these acids are distilled, they yield carbonic acid; two liquid carbo-hydrogens, oleéne and elaéne, both having the composition of olefiant gas; and an empyreumatic oil. (Fremy.)

The two carbo-hydrogens are separated by careful rectification. Oleéne, the more volatile, boils at 131°, has an alliaceous smell, is very combustible, and appears to have poisonous properties. Elaéne boils at 230°, has a smell like that of oleéne, and is decomposed by chlorine with the production of hydrochloric acid, and a new liquid compound.

Fremy adopts for metoleic acid the formula $C_{70}H_{63}O_{8},HO$; but the analysis of the salt of silver rather indicates that it is a bibasic acid, and that its formula is $C_{90}H_{85}O_{10},2HO$. This formula readily explains the action of heat; for if from 1 at. of the hydrated acid $= C_{90}H_{87}O_{12}$ we subtract 5 at. of carbonic acid and 2 of water $= C_{5}H_{2}O_{12}$
there will remain $C_{85}H_{85}$. This may be divided into $C_{40}H_{40} =$ oleéne, and $C_{45}H_{45} =$ elaéne. The calculated density of elaéne in the state of vapour agrees with Fremy's experiment. The compound formed by chlorine seems to be $C_{45}H_{40}Cl_{5}$, in which 5 at. of hydrogen are replaced by 5 of chlorine.

According to Fremy, hydroleic acid only differs from metoleic acid in containing the elements of 1 at. of water more. This admits of the same explanation of the action of heat, which is the same in both acids.

2.—ACTION OF NITROUS ACID ON OILS.

It has already been stated, under the head of oleic and elaidic acids, that oleic acid is solidified by nitrate of mercury or nitrous acid. Poulet first observed this action in the case of olive oil and several other oils. Boudet showed that nitrous acid is the true agent, and that oleine (oleate of oxide of glycerule) is converted by it into elaidine, a solid fat, which is composed of elaidic acid and oxide of glycerule.

When olive oil, for example, is mixed with the common red fuming nitric acid of commerce, it is solidified by the nitrous acid present. According to the quantity of nitrous acid, the change is effected in a longer or shorter time. When a mixture of 3 parts pure nitric acid and 1 part hyponitrous acid (produced by the distillation of nitrate of lead,) was used, the following results were obtained:

1 part of the acid mixture with	33	of olive oil solidified in	70 minuets.
1	50		78
1	75		84
1	100		130
1	200		435
1	400 remained unchanged.		

The very small quantity required to produce the effect, and the fact that in several oils, castor oil for example, a similar solidification is caused by sulphurous acid, render this action a problem which is yet unresolved.

Oil of almonds, of acacia nuts, of rape seed, castor oil, and oil of hazel nuts, agree with olive oil in being solidified by nitrous acid or nitrate of mercury. The oils of linseed, hemp, walnuts, poppy seed, and other drying oils, undergo no change when mixed with these reagents, except that they are coloured brown. The presence of drying oils prevents or retards the solidification of the fat oils.

The product of the action of nitrous acid on the fat oils is the same in all cases, except in that of castor oil. A yellowish semi-solid mass is formed, which when washed with alcohol becomes white, and when further purified by pressure and crystallization is pure elaidine. The yellow matter taken up by the alcohol changes to a dark brick-red by the action of alkalies.

Those oils which yield elaidine, generally contain margarine and oleine. It is at present doubtful whether the former in these circumstances yields a part of the elaidine; for pure margaric acid cannot, like oleic acid, be converted into elaidic acid. The elaidine from almond oil appears to contain oleine, and that from olive oil margarine. If this be really the case, the purest elaidine yet obtained cannot be considered as pure elaidate of oxide of glycerule. Pelouze and Boudet, however, state that when margaric acid is dissolved in oleic acid, both are entirely converted into elaidic acid. This requires confirmation.

The oleine of human fat and of hog's lard, as well as that of the oils above-mentioned, is converted by nitrous acid into elaidine. But neither the solid part of these and other fats, pure stearine, nor pure stearic acid, can be made to undergo this change.

Elaidine made from olive oil melts at about 90°. When saponified, the soap treated with acids yields elaidic acid, which is probably impure, as it melts at 107° and lower; while pure elaidic acid, made from pure oleic acid, melts at about 112°. Laurent analyzed the acid from olive oil, and has given the formula $C_{70}H_{78}O_6$. But, till we are satisfied of its purity, this formula cannot be adopted.

Palmine.—Castor oil, when treated with nitrous acid, yields a peculiar new fat, palmine, which melts at 143°. When saponified by alkalies, it yields oxide of glycerule, and a new fatty acid, palmic acid.

Palmic Acid.—The soap made from palmine and potash being purified, is decomposed by tartaric acid, and the fatty acid which separates is dissolved in cold alcohol. The solution, by spontaneous evaporation, yields pure hydrated palmic acid. It is crystallizable, and melts at 122°; it is very soluble in alcohol and ether. When boiled with alcohol, it seems to form palmate of oxide of ethule; at least, an oily liquid separates on cooling. It is partially decomposed by distillation. Its salts are little known; and the composition both of palmine and palmic acid is yet undetermined.

It is very remarkable that a current of sulphurous acid gas, when passed through castor oil, converts it into a solid mass, which seems to be palmine, and which, when saponified, yields palmic acid. That the same acid should be formed by an oxidizing and a deoxidizing agent is a fact which requires a careful investigation.

ACTION OF METALLIC OXIDES ON FIXED OILS AND FATS.

The action of alkalies and of oxide of lead on fixed oils and fats has long been practically known. The compounds produced by the former are called *Soaps:* those formed by oxide of lead are *Plasters.*

Up to 1813 soaps and plasters were considered to be compounds of alkalies and oxide of lead with oils and fats; although it was observed that the oil, when again set free, had acquired a greater solubility in alcohol, and was more readily saponifiable than before. The discovery of glycerine by Scheele was the only well-ascertained fact previous to the researches of Chevreul in 1813.

This illustrious philosopher observed that a certain kind of soap, when diluted with a large proportion of water, became turbid, and deposited a pearly substance, which he found to contain an alkali combined with an oily matter, not previously described, of decided acid properties. This observation was the origin of, perhaps, the most splendid series of investigations known in the history of chemistry; in the course of which, continued as they were for fourteen years, Chevreul not only discovered a large number of new compounds, and cleared up the whole subject of the fixed oils, fats, soaps, and plasters, but established those principles which at present prevail in the study and analysis of organic substances.

At a time when such investigations were unknown in organic chemistry, the profound sagacity of this distinguished philosopher taught him that the ultimate analysis of an organic compound was not alone sufficient to determine its true composition; but must be accompanied by a complete study of the changes produced on it by the action of reagents, and a careful determination of the quantities of the several products as well as of their composition.

This great principle, which now regulates all researches in organic chemistry, we owe to Chevreul. By it he was led to numerous discoveries, and by it also he was guarded from error, at a time when all was error in this branch of chemistry. But the example of Chevreul was not immediately followed; and it was not till Dumas and Boullay, in 1824, applied the same principle to the study of the ethers, that its application to organic chemistry in general gave rise to the extraordinary progress which, since that time, has been made in this department of the science.

Chevreul showed that the different kinds of fixed oils and fats contained three distinct compounds, united in the most various proportions: one, liquid at ordinary temperatures, which he called Oleine; and two solid, but differing in fusibility, Stearine and Margarine.

He also showed that each of these contained oxide of glycerule, (glycerine,) in combination with an oily acid; and that when the oil or fat was acted on by alkalies, or by oxide of lead or zinc, these bases united with the oily acids,—forming, in the first case, soluble soaps; in the other, insoluble plasters. The oxide of glycerule in the moment of separation united with water, forming hydrated oxide of glycerule (glycerine, or sugar of oils). When the weight of the glycerine was added to that of the oily acids, after the latter were separated from the bases, their united weights exceeded somewhat that of the original oil; which he showed to arise from the fact, that both the oily acids and the glycerine, when separated from other substances, combine with water. With ordinary oils and fats no other products are formed; but when the oil or fat contains any of the volatile oily acids, such as butyric or phocenic acids, the soap contains a salt of the volatile acid, and acquires its smell.

Soaps are divided into *hard* and *soft soaps.* The former are obtained from fats or fat oils; the latter from drying oils. Of the hard soaps, those containing soda are firmer than the soaps of potash. Of the hard soaps of commerce, those made with vegetable oils are mixtures of oleate and margarate of potash or soda; those made with animal fats are mixtures of stearate, margarate, and oleate of potash or soda.

In order to form soap, the oil or fat is boiled with a solution of caustic potash or soda, till the whole forms a thick viscid emulsion, which can be drawn out into long clear threads. If not clear, either water or alkali must be added, according as the turbidity depends on undecomposed oil, or on a deficiency of water. When the saponification is complete, the next step is to separate the soap from the excess of alkali, the glycerine, and the superfluous water. This may be effected by boiling down till the alkaline ley becomes very concentrated, when the soap becomes insoluble, and rises to the surface. The same end is attained by adding very strong ley, or common salt, both of which render the soap insoluble when added in sufficient quantity; soap being absolutely insoluble in alkaline ley of a certain strength, as well as in a saturated solution of common salt. The separation is known to be complete when the liquid ceases to froth in boiling; and the soap is ladled off into moulds, where it is well stirred to favour the separation of the liquid, which should run off from its surface like water from fat. The soap brought to this state in the first operation is called *grain soap,* from its separating in grainy particles at first. It may be further purified by repeating the process of dissolving it in alkaline ley, and separating it by the addition of salt. In this process the impurities subside, and the soap generally takes up more water; so that, although whiter, it is less strong. White soap, for example, commonly contains 45 to 60 p. c. of water, while grain soap only contains 25 to 30 p. c. No doubt it might be again procured with as little water as at first; but it is the fluidity caused by the additional water that allows the impurities to subside, and the soap to become white. What is called marbled soap is grain soap which has not been subjected to purification; and the grey, blue, and green colours in it arise principally from the presence of insoluble soaps of oxide of iron or of copper.

It is to be observed, that when common salt is added to the solution of a soap of potash, the latter is converted into soda soap, entirely or partially, according to the quantity of salt, while chloride of potassium is formed. As this latter salt does not cause the soap to separate, like common salt, it is necessary to use twice as much salt to separate the soap when it has been made with potash. If a soap of potash be required, it must be separated by caustic potash. In Germany soda soap is first made with potash, and the potash soap is decomposed by common salt. In England and France, soda soap is made directly with caustic soda.

The use of salt in this important process depends on the curious fact, that soap, like muscular fibre or animal membrane, cannot be moistened by a saturated solution of salt; that is, cannot deprive it of water. On the other hand, if these substances be moistened with water, or dissolved in it, the addition of dry salt in sufficient quantity will remove the whole of the water.

Soft soaps are made with drying oils, either alone, or mixed with train oil or other fat oils. They are insoluble in strong alkaline ley, and are separated from water by the addition of potash or soda. When train oil is added, they have the disagreeable smell of that oil, arising from phocenic acid.

Such is a very general and brief account of the principles of soap-making, which are few and simple. The great experience of the makers of a substance so long known had taught them empirically how to produce good soap in a great variety of forms; but it is only of late that the rationale of their processes has been understood, and that improvements have been made on scientific principles. Soap-making may now be considered as one of the arts most thoroughly understood.

It is impossible here to describe the varieties of soap. Of the simple soaps, stearate of soda may be considered the type of hard soaps. It is hardly altered by contact with 10 parts of water. Stearate of potash, with 10 parts of water, forms a viscid solution. The margarates of soda and potash resemble the stearates. Oleate of soda dissolves in 10 parts, oleate of potash in 4 parts of water. Hence soaps are harder and less soluble, the more stearate and margarate they contain; and softer and more soluble when oleates predominate.

As the soaps of lime, baryta, earths, and metallic oxides in general are insoluble, the use of hard water, which contains salts of lime, causes a precipitation of the insoluble soap, which is very prejudicial. This may be corrected by adding to the water as much carbonate of soda or potash as is sufficient to separate all the lime, before the water is used to dissolve soap. It is in this way that soda renders hard water soft for washing and other purposes.

The soap used in medicine is a hard soap made by boiling to dryness in a gentle heat 1 part of soda ley, sp. g. 1·33, and 2 parts of olive or almond oil. It is a mixture of margarate and oleate of soda with free soda and glycerine. *Antimoniated soap* is made by dissolving 1 part of precipitated sulphuret of antimony in caustic potash, mixing the solution with 6 parts of medicinal soap, and evaporating to dryness.

PLASTERS.

There are two kinds of officinal plaster made with lead,—litharge plaster, and white lead plaster; but all the compounds of oxide of lead with the oily acids possess the properties of plaster.

Litharge plaster, or Diachylon plaster, is made by boiling 5 parts of levigated litharge (protoxide of lead) with 9 of olive oil, and some water, till the whole acquires a proper consistence and a greyish white colour. At common temperatures it is plastic; when heated, it melts. It may also be obtained by adding subacetate of lead to a solution of soap. The plaster thus formed is good at first, but afterwards becomes hard; while that prepared directly from the oil remains plastic, apparently from the presence of undecomposed oil. Litharge plaster consists chiefly of basic oleate and margarate of lead. It is the basis of almost all medicinal plasters.

White lead plaster (Emplastrum cerussæ) is made in the same way, using 16 parts of carbonate of lead to 9 of olive oil. It is white, plastic in the heat of the hand, liquid at 212°. It enters into the composition of many plasters used in medicine.

Iron plaster and *Mercurial plaster* are made by adding salts of mercury or iron to solution of soap. They are insoluble masses, softened by heat, and are not much used.

OILS AND FATS OCCURRING IN NATURE.

1.—DRYING OILS.

The drying oils are generally derived from seeds by pressure. Their distinguishing character is that of drying into a varnish by exposure to the air. This change is caused by the absorption of oxygen; and, as the impurities generally present in oils impede the access of oxygen to the particles of the oil, the drying takes place much more rapidly when these impurities are removed or destroyed. Boiling acts by destroying them, and a little litharge is added to promote the change. But a better and more colourless varnish is obtained by agitating the drying oil, linseed oil for example, with a mixture of water, litharge, and subacetate of lead, without heat. When the whole is allowed to stand, the impurities subside with the water, and the oil is so pure that it dries into a varnish in twenty-four hours. It contains a little oxide of lead, but this rather improves the varnish.

The absorption of oxygen by drying oils goes on so rapidly when their surface is much extended, that wool, shavings, tow, or other porous substances, when steeped in drying oil and exposed to the air, often take fire spontaneously from the heat developed. This is a frequent cause of fire in manufactories, where the oiled parts of the machinery are wiped with tow or cotton.

The oil or varnish for printer's ink is made by boiling drying oil till it acquires the proper consistence, and the tendency to dry quickly.

The following are the principal drying oils: —*Linseed oil*, from the seeds of *Linum usitatissimum*. It has the properties of drying oil in the highest degree. *Walnut oil*, from the kernel of the walnut, *Juglans regia*. This oil stands next to the preceding as a drying oil. *Hempseed oil*, from the seeds of *Cannabis sativa*. *Oil of Poppy-seed*. *Croton oil*, from the seeds of *Croton tiglium*. The oils of *Jatropha multifida* and *Jatropha curcas*, resembling croton oil in activity and other properties. The oils of *Euphorbium lathyris* and of *Cucurbita pepo* are also drying oils.

2.—FISH OR TRAIN OIL.

Under the name of train oil several varieties of fish oil are known. They have some resemblance to the drying oils; but are distinguished by containing, in general, one or more volatile oily acids in small quantity, generally phocenic acid. They are for the most part composed of oleine with a little phocenine. The principal varieties are whale oil, seal oil, dogfish oil, and cod's liver oil. Most fish oils contain a small quantity of a crystallizable fatty acid, not yet examined. That of the dolphin holds a portion of spermaceti dissolved. Fish oil is used for lamps, and to mix with drying oils for soft soap.

3.—LIQUID FAT OILS.

These are distinguished from the drying oils by the action of the air; if exposed to it, they are slowly altered, but remain greasy and do not yield a dry varnish. They are used both as food and for burning. They are purified from foreign matters by being agitated with a little oil of vitriol, and afterwards washed with water to remove any adhering acid. After this operation they burn much more brightly, and clog the wick much less. They are all more or less completely solidified by nitrous acid, which is not the case with drying oils.

The principal fat oils are *olive oil*, from the pulp of the olive, *Olea Europœa*, which is much used as an article of food, and for making soap. It congeals when exposed to cold, and the solid portion seems to be a compound of margarine and oleine. *Almond oil* contains much less margarine than olive oil. It therefore yields softer soap, and is better adapted to the preparation of oleic acid. *Rapeseed oil* and *Oil of Colza* are similar to olive oil, and much used as combustibles on the Continent.

The *Oil of yolk of egg* and *Oil of cow-heel* are two mild inodorous animal oils, very similar to vegetable oils. The former soon becomes rancid; but the latter, from retaining its sweetness very long, is much prized for fine salves and ointments.

4.—SOLID FAT OILS, OR FATS.

These are numerous both in the vegetable and animal kingdoms, and are known by various names, such as tallow, suet, lard, butter, and fat.

Laurel fat is obtained from laurel berries by boiling and pressure. It is green and soft, and is used for salves.

Butter of Cacao, from the beans of *Theobroma cacao*, is white, solid, and rather brittle. It does not become rancid; the greater part of it is a crystalline compound of oleine and stearine, melting at 85°.

Butter of Nutmegs, from the nuts of *Myristica moschata*, is solid, yellow, and possessed of the aromatic smell of the essential oil of nutmegs. Cold alcohol dissolves a fat oil, the essential oil, and the colouring matter; leaving 25 to 30 p. c. of a white crystalline fat, fusible at 87°. This fat resists the action of diluted alkalies, but is quickly saponified by fusion with hydrate of potash. The soap thus formed yields a crystallizable acid, fusible at 122°. This is sericic acid; and the fat is sericate of oxide of glycerule, or sericine. (Playfair.)

Butter of Cocoa-nuts, from the fruit of *Cocos nucifera*, is white and soft, fusible at 68°, and consists of two oils, one liquid, the other solid, at ordinary temperatures. The latter, according to Pelouze and Boudet, is identical with *elaidine*. This butter soon becomes rancid.

Palm oil or butter, from the rind of the fruit of *Avoira elais*, *Elais Guianensis*, is yellow and semi-solid, with a smell of violets. When new, it melts at 81°; when long kept, at 90° to 96°. It easily becomes rancid, glycerine being set free, and at the same time the fatty acids. It contains oleine, margarine? and about two-thirds of its weight of a white solid fat, which is palmitine, and which contains palmitic acid. (Fremy, Stenhouse.) Palm oil is much used for making soap. If white soap is desired, the oil must be bleached; which may be done either by exposure to the sun, by sulphuric acid, or by chlorine. Tallow is added to increase the firmness of the soap. For yellow soap, resin is added to the palm oil.

Galam butter, from *Bassia butyracea*, is often confounded with palm oil. It is softer and more fusible, and is equally liable to rancidity.

There are some other kinds of vegetable butter, which, however, are too little known to be accurately described.

Tallow.—This name is given to the fat of oxen, sheep, deer, and goats. They all consist chiefly of stearine with a little oleine; but the last-named contains also hircine (hircate of oxide of glycerule) in small quantity, to which it owes its peculiar smell. They form, with soda, firm hard soaps; and are much used, not only for soap-making, but for ointments and plasters, and in making candles. Tallow soon becomes rancid on exposure to the air. The fat of *ox-marrow*, having very little tendency to rancidity, is used for salves and pomatums.

Butter, derived from the milk of the cow, is a soft yellowish fat, which may be purified from buttermilk, cheese, and the other impurities it contains, by melting it; when the water subsides, and the pure oil rises to the surface. It should be repeatedly melted with water. It consists of margarine, oleine, butyrine, caprone, and caprine. The three latter are compounds of oxide of glycerule with the volatile butyric, caproic, and capric acids. (Chevreul.) Their quantity is small, but to them are owing the peculiar pleasant taste and smell of fresh butter. Butter soon becomes rancid: hence the necessity of either procuring it always fresh, or of salting it. When purified as above, it keeps much longer, but is much less pleasant to the taste. If melted butter be poured into ice-cold water, it assumes the consistence of fresh butter.

Rancid butter, like other rancid fats, may be in a great measure deprived of rancidity by melting and shaking it repeatedly with twice its weight of boiling water. Fresh butter, when laid in syrup, keeps even better than salted butter.

Hog's-lard, or *Axunge*, is softer than tallow. It contains more oleine, and probably margarine along with the stearine, or in place of it. It is chiefly used for ointments.

Human fat appears to contain no stearine, but only margarine and oleine.

Spermaceti.—This remarkable fat is found in certain cavernous receptacles in the head of several species of *Physeter* and *Delphinus*. During the life of the animal, it is dissolved in spermaceti oil; but, after death, it is deposited on cooling in a crystalline mass. It consists chiefly of cetine, which is contaminated with an oil soluble in cold alcohol.

Cetine. — To obtain it pure, spermaceti is dissolved in boiling alcohol, which on cooling deposits the cetine in crystals. The process is repeated as long as the alcohol extracts any oil. Pure cetine is crystalline, has a bright pearly lustre, and melts at 120°. At 670° it sublimes undecomposed. If distilled at a higher temperature, it yields inflammable gas, a mixture of margaric and oleic acids, and an oil insoluble in alkalies, but no ethal (hydrated oxide of cetule).

When saponified by fusion with caustic potash, it yields oleate and margarate of potash, and ethal; the latter amounting to 40·64 p. c. According to Dumas, cetine contains 2 at. of margaric acid, 1 at. of oleic acid, and 3 at. of oxide of cetule ($C_{32}H_{33}O$). But as margaric and oleic acids, in the above proportions, and adopting the formula of Chevreul, neutralize 4 atoms of base, while only 3 atoms are here present, it is probable that 1 at. of basic water should be added to the formula of Dumas. Moreover, it has not been proved satisfactorily that the acids in cetine are identical with common margaric and oleic acids; so that the formula of cetine must be considered as doubtful.

Cholesterine or *Fat of Bile.* — This fat is found in the blood, the brain, and the bile of animals. It is the chief ingredient of biliary concretions, from which it is readily obtained by solution in boiling alcohol, which on cooling deposits the cholesterine, retaining in solution the small portion of colouring matter which it dissolves. Any fatty acids which may contaminate it are easily removed by potash.

It forms large pearly or silvery scales, insoluble in water, fusible at 279°, and volatilizable in close vessels, without change. It is not saponified nor dissolved by caustic alkalies; and it appears to be dissolved in the serum of the blood by means of soap, stearate of soda being present in that fluid. Wagner has shown that 4 parts of soap, dissolved in water, take up one part of cholesterine.

The analyses of cholesterine, by Chevreul, Couerbe, and Marchand, indicate either the formula $C_{38}H_{33}O$ or $C_{36}H_{32}O$. A knowledge of its atomic weight can alone decide between these formulæ.

Cholesteric Acid.—By boiling with nitric acid, cholesterine is converted into cholesteric acid. This acid forms pale yellow needles, lighter than water, very soluble in ether. It forms red salts; those with the alkalies are soluble, the rest insoluble. Its formula is unknown, but it contains nitrogen, derived from the nitric acid. (Pelletier and Caventou.)

Ambreine. — This is a substance closely allied to cholesterine. It occurs in ambergrise, a peculiar fat found floating on the sea in the southern latitudes, and supposed to be a concretion formed in the stomach of the spermaceti whale. From ambergrise ambreine is obtained, exactly as cholesterine is from biliary calculi. By the action of nitric acid it is converted into an acid, *ambreic* *acid,* analogous to cholesteric acid, and, like it, containing nitrogen.

Castorine.—This is a crystallizable substance, analogous to the two preceding; which is extracted, along with common fat, from castor (castoreum) by the action of alcohol. It dissolves unchanged in alkalies, and is converted by nitric acid into an acid analogous to ambreic acid. (Brandes.)

WAX.

This substance, or a substance closely resembling it, is found in many plants, particularly in the pollen. It is collected by bees to build their combs; but it is not determined whether these animals possess the power of producing it from sugar, or any other portion of their food.

As obtained by melting honeycomb with water, it is yellow, and has a peculiar smell. It melts at 145°. When exposed in thin layers, or ribbons, to the action of light, it is bleached, and deprived of smell. When bleached, it melts at 158°, and congeals at 149°.

According to the researches of Gay-Lussac and Thenard, Chevreul, Saussure, Ettling, and others, wax is a mixture of two substances in very variable proportions. One of these is very soluble in hot alcohol, the other very sparingly soluble in that menstruum. The former is cerine, the latter myricine.

Cerine is deposited in a gelatinous mass, composed of fine needles, from the alcohol on cooling. When boiled with potash, it is partially saponified, and the soap appears to contain margaric and oleic acids. There is obtained at the same time about 56 p. c. of a neutral substance; insoluble, or nearly so, in alcohol, and unchanged by boiling with potash. This is *ceraine.* It seems to have the same composition as the portion of wax insoluble in alcohol.

Myricine.—This is the matter left undissolved when wax is boiled with alcohol. It requires 200 parts of boiling alcohol for solution, and is not affected by boiling with caustic potash.

The formulæ of these compounds are not ascertained; but the analyses of Ettling and Hess show that cerine contains more oxygen than myricine; while the composition of ceraine and myricine appears to be the same.

Some species of vegetable wax appear to be composed of myricine alone, others of cerine; while the so-called wax of *Myrica cerifera*, when saponified, yields stearic, margaric, and oleic acids, along with glycerine, and is therefore rather fat than wax. Bees' wax varies very much in the proportions of myricine and cerine which it contains.

When wax is distilled, it yields a fatty acid, not yet examined; an oil composed of carbon and hydrogen in the same proportions as olefiant gas; and a solid white crystallizable substance of similar composition, which is identical with paraffine. Neither sebacic acid nor acroleine appears among the products.

Japan or *Tree Wax*, from the fruit of *Rhus succedanea*, resembles wax in appearance, but appears to be more of the nature of fat. It is easily saponified, and yields an acid which is either margaric acid, or one analogous to it. Substances more or less similar to wax are obtained also from *Croton sebiferum*, *Celastrus ceriferus*, and *Ceroxylon andicola*. They are as yet little known.

Cerosine. — Some species of sugar-cane yield on the surface of the cane a waxlike substance, which has been examined by Dumas, who has given to it the above name. It forms fine light pearly scales, fusible at 180°, and is not saponified by potash. The analysis of it by Dumas led him to the formula $C_{48}H_{50}O_2$.

APPENDIX.

ORGANIC ACIDS, HITHERTO LITTLE EXAMINED.

Chelidonic Acid.—This acid was discovered by Probst in *Chelidonium majus.* It forms small white crystals, very acid to the taste, sparingly soluble in cold water, soluble in 26 parts of boiling water. The analysis made by Probst leads to the formula $C_7H_2O_3$, which seems to indicate some relation to meconic acid, which occurs in the same natural family of plants, the Papaveraceæ.

Caincic Acid. — This acid occurs in the root of several species of *Chinococca.* Formula, $C_8H_7O_4$? (Liebig.) It is crystallizable, and has at first little taste, but soon developes an acrid bitterness. It is sparingly soluble in water and ether, more soluble in alcohol.

Crameric Acid.—This acid is found in rhatany root, said to be the root of *Crameria triandra;* but some commercial specimens do not yield it. It is crystallizable, soluble in water, and has a sour astringent taste. It is remarkable for its strong affinity to baryta. It is even capable of depriving sulphate of baryta of that earth; and the cramerate of baryta is not decomposed, either by sulphuric acid, or by soluble sulphates. Its composition is unknown.

Caffeic and *Tanno-caffeic Acids* were discovered by Runge in coffee. The former is a white powder, which when heated yields the aromatic odour of roasted coffee. The latter is a variety of tannic acid, producing in salts of iron a green precipitate.

Boletic Acid. — Discovered by Braconnot in the fungus *Boletus pseudo-igniarius.* It is crystallizable and volatile, and precipitates peroxide of iron completely from its solution.

Fungic Acid occurs, according to Braconnot, in most fungi. It does not crystallize, is deliquescent, and has a very sour taste.

There are several other acids, the existence of which as distinct compounds is still problematical: such are, Tanacetic Acid, in *Tanacetum vulgare;* Lactucic Acid, in *Lactuca virosa;* Atropic Acid, in *Atropa belladonna;* Cocognidic Acid, in the seeds of *Daphne gnidium;* Solanic Acid, in the different species of *Solanum;* Coneic Acid, in *Conium maculatum;* Aceric Acid, in *Acer campestre; Moroxylic Acid*, in the wood of the Mulberry; Kinovic Acid, in the Chinanova Bark; Menispermic Acid, in Cocculus Indicus, which is the seed of *Menispermum Cocculus*,—an acid said to exist in the silkworm; &c. &c. It is probable that most of these acids, when properly investigated, will be found identical with some one or other of the acids previously described.

OF THE VOLATILE OR ESSENTIAL OILS.

Many vegetable products, when distilled with water, yield essential or volatile oils, which are liquids, more or less volatile, sparingly soluble in water, generally colourless, although occasionally having a peculiar tint, and for the most part possessing the entire odour of the plant. They are inflammable, burning with a bright but smoky flame, and undergo peculiar changes by the action of air and water.

Analogous to these are the so-called empyreumatic oils, which are among the products of the destructive distillation of organic matter.

Many of the essential oils exist ready formed, and in the free state, in certain parts of plants; as, for example, in the rind of the orange and lemon, from which they may be obtained by mere pressure. Others flow from incisions in the plant, combined with resin, forming what are called Balsams; as is the case with oil of turpentine. In several cases it has been proved, that the oils are first formed by the mutual action of two or more organic compounds when the plant is placed in contact with water: this is the case with the oil of bitter almonds, and with oil of mustard, and is true of all the volatile odoriferous oily matters formed during fermentation or putrefaction. (See ante, Amygdaline.)

It thus happens that perfectly inodorous plants, as, for example, *Centaurium minus*, when allowed to ferment with water, and then distilled, yield a penetrating essential oil.

The essential oil of *Spiræa ulmaria* may be obtained, with all its characteristic properties, from salicine, by the use of oxidizing agents (see Hyduret of salicule); and finally, when starch or sawdust and similar substances are heated with sulphuric acid, peroxide of manganese, and water, they yield, besides formic and carbonic acids, oily liquids possessing all the characters of essential oils.

In some fragrant flowers, as the lime blossom, jonquil, and jasmine, the odorous principle may be extracted by ether or by fixed oil, but cannot be obtained by distillation with water; either because it is decomposed, or else is so soluble that it cannot be separated readily from the water. In the latter case, it may sometimes be separated by saturating the water with common salt.

Many essential oils contain a crystalline substance dissolved, to which the name of Stearopténe is given. This in numerous cases, as in the oils of lavender and valerian, is pure camphor. Others contain volatile oily acids mixed with a neutral oil, as is the case in oil of cloves; and many contain nitrogenized compounds, such as ammonia and hydrocyanic acid.

Their specific gravity varies; some are heavier, others lighter than water.

Some contain no oxygen; while in others that element is present. It is worthy of especial notice, that all the non-oxygenated essential oils as yet accurately analyzed contain carbon and hydrogen in the same relative proportions, expressed by the empirical formula $C_{10}H_8$. With widely different properties, they yield the same result, as to these elements, in 100 parts. There can be no doubt that in many cases the true formula is a multiple or submultiple of the above. In others, the arrangement of the same number of equivalents may vary.

The oxygenated essential oils are commonly mixtures of several, differing in volatility; but, as no one has succeeded as yet in effecting their complete separation in any case, the analyses of them which have been made are of no value.

All essential oils are miscible with alcohol; and they are more soluble in weak spirits, the more oxygen they contain. To water, although sparingly dissolved by that liquid, they give their peculiar odour, forming what are called *distilled waters*. When these are made by distilling the plant with water, they are apt to mould, from the presence of foreign matter; but, if distilled a second time, they keep well in close vessels.

It must here be observed, that the odour of these oils is closely related to their alteration by air and water. They almost all absorb oxygen, and those which do so most rapidly have the strongest smell. If non-oxygenated oils be distilled with quicklime in vacuo, or in an atmosphere of carbonic acid, the product is absolutely inodorous; and it is impossible in this state to discriminate oil of lemons from oil of turpentine or of juniper: but, when exposed to the air, they quickly become odorous, while they absorb oxygen, becoming viscid and resinous. It would appear, therefore, as if the odour accompanied the act of oxidation, as is the case with metallic arsenic. By long exposure to the air, these oils gradually acquire the aspect of resins. Many become acid which before were neutral: the acid in oil of cinnamon is cinnamic acid; in oil of bitter almonds it is benzoic acid; and, according to Bizio, in some cases it is acetic acid. It is probable that the resins formed by the oxidation of essential oils are identical with those which in the balsams accompany the oils; but on this point we have no experiments. According to Saussure, carbonic acid is one of the products of the action of the atmosphere on essential oils.

It is not probable that these oils act as radicals, combining with oxygen directly to form the resins; it seems more likely that the oxygen removes one portion of their hydrogen, while the remainder of the hydrogen resists the action of oxygen, chlorine, and iodine much more strongly.

All the non-oxygenated oils, in contact with iodine, yield a part of their hydrogen with a kind of explosion, while iodine replaces the hydrogen thus removed. The new compound, although rich in hydrogen, does not yield any more to an additional quantity of iodine. The action of both oxygen and chlorine is analogous: both remove a part of the hydrogen; both also enter into the new compound, replacing that element; so that the new body, the resin, for example, always contains less hydrogen than the oil.

By strong nitric acid the essential oils are converted into resinous matters, as yet little studied. Many oils burst into flame when mixed with nitric acid, especially if a little sulphuric acid be previously added to it. When boiled with moderately strong nitric acid till dissolution ensues, the oils yield peculiar crystallizable acids, but no oxalic acid.

The essential oils dissolve sulphur and phosphorus, and are miscible with bisulphuret of carbon and hydrated acetic acid.

We shall now briefly describe the individual oils, and their relation to other substances. The whole subject is but imperfectly known; and a profound and searching investigation is required, not only of their composition, but also and chiefly of the changes they undergo by the action of oxygen, chlorine, iodine, &c. before we can hope to acquire a knowledge of their true nature and constitution. Oil of turpentine and oil of lemons, for example, are both composed according to the empirical formula $C_{10}H_8$. The latter may be $C_{10}H_7 + H$; the former $C_{20}H_{15} + H$. It is obvious that the decision of these and similar questions cannot be expected from mere analyses of the oils, however accurate.

1. NON-OXYGENATED ESSENTIAL OILS.

Oil of Turpentine.—Turpentine, which is a semi-fluid mass, flowing from incisions in the wood of many species of Pinus, and which is a good type of the balsams, yields the oil in question when distilled with water. The oil of commerce, from exposure to the air, is always contaminated with resin. To purify it, it is again distilled with water, dried by chloride of calcium, and rectified. It is then clear, colourless, very mobile, and has a very pungent peculiar smell and a burning taste. It sp. g. is 0·86 to 0·87. When pure, it is neutral to test paper. It boils at 312°, and the density of its vapour is 4·764. (Dumas.) It is almost insoluble in water, but communicates to that liquid its smell. When moist, and left long in the cold, it often yields a solid crystalline hydrate, in which to $C_{10}H_8$ there are 2 at. water, (Blanchet and Sell,) or 3 at. (Dumas and Peligot.) This hydrate is soluble in 22 parts of hot water, and crystallizes on cooling. The oil is very soluble in alcohol, ether, and fixed oils. Being less soluble in weak spirits, it may be freed from resin by agitation with a little proof spirit. It is instantly decomposed by sulphuric or nitric acid, and takes fire with a mixture of the two. Chlorine also acts on it rapidly, and with flame, if the quantity of oil be small in proportion to the gas. By the slow action of chlorine, one fourth of the hydrogen is removed, and replaced by chlorine; and a similar effect is produced by bromine and iodine. It dissolves sulphur and phosphorus.

Pure oil of turpentine contains no oxygen. In 100 parts it is composed of

Carbon	88·46
Hydrogen	11·54

which corresponds to the formula $C_{10}H_8$.

With hydrochloric acid gas it forms a liquid and a solid compound. The former is volatilizable, colourless, soluble in alcohol and ether. The vapour of this compound, passed over hot lime, yields chloride of calcium and an oil of the same composition as oil of turpentine. This has been called Peucyl, or Peucylene. Its sp. g. is 0·86, and it boils at 273°.

The solid compound may be purified by sublimation and crystallization from alcohol. It is white, translucent, lighter than water, insoluble in water, soluble in alcohol. Its solution does not precipitate nitrate of silver.

Its empirical formula is $C_{20}H_{17}Cl$. By repeated distillation of its alcoholic solution over hydrate of lime, the hydrochloric acid is at last removed; and it yields another oil of the composition of oil of turpentine, called Dadyl, Terebene, or Camphilene. Its sp. g. is 0·86, and it boils about 300°. According to Dumas, who considers it to be pure oil of turpentine, and calls it Camphene, its true formula is $C_{20}H_{16}$, as deduced from the action of chlorine upon it. The results of Soubeiran and Capitaine, and of Deville, confirm this view.

The last-mentioned oil, when brought in contact with hydrochloric acid gas, reproduces the crystalline compound above-mentioned which has long been known as Artificial Camphor. According to Blanchet and Sell, oil of turpentine is a mixture of two oils, Peucyl and Dadyl, which have the same composition, and of which the former gives with hydrochloric acid a liquid, the latter a solid compound.

By the action of nitric acid, oil of turpentine is first converted into a resinous mass, which by long boiling with the acid is at last dissolved, and converted into a crystalline acid, Turpentinic Acid. According to Bromeis, its formula is $C_{14}H_9O_7,HO$. It merits a careful investigation.

Oil of turpentine is used in medicine both internally and externally. It is also much used in the arts for dissolving resins and oils in making varnishes.

Oil of Juniper.—Obtained from the berries of *Juniperus communis* by distillation with water. The unripe berries yield most oil; and this oil is a mixture of two, differing in volatility, as one boils at 310°, and the other at 400°. Both have the odour of juniper; and both, when agitated with a solution of salt, form crystalline hydrates. The more volatile portion has the same composition in 100 parts as oil of turpentine, and forms with hydrochloric acid gas a liquid compound, the formula of which appears to be $C_{15}H_{13}Cl$, according to Souberian and Capitaine, who call the supposed radical of this compound Juniperiléne.

The addition of a little oil of juniper to brandy forms gin, or geneva. Both this and the oil are used as diuretics, and give to the urine the smell of violets.

Oil of Sabine, from the berries of *Juniperus Sabina*, resembles the preceding, has the same composition, and is also used as a diuretic. Its smell, however, is disagreeable.

Oil of Elemi, from the resin of *Amyris elemifera* and *A. ceylanica*, is colourless, has a pleasant smell, the sp. g. 0·852, and boils at 330°. Its other properties resemble those of oil of turpentine, except that it does not produce artificial camphor with hydrochloric acid gas, which colours it brown. It has the composition of oil of turpentine; and its formula is C_5H_4, or a multiple of this.

Oil of Storax, obtained from *Storax liquida* by distillation with water, is colourless, and has the smell of the balsam. According to Marchand, it has the same composition as benzine, C_2H, or some multiple of it.

Nitric acid, by the aid of heat, converts it into a resinous mass, which, when distilled with water, yields a pungent oil with an odour of cinnamon, which crystallizes on cooling, and by solution in hot alcohol may be obtained in fine crystals. (Simon.) This is Nitrostyrole. Its formation is accompanied by that of benzoic and hydrocyanic acids.

The oil of storax itself, called by Simon Styrole, when exposed to the air, absorbs oxygen, and is slowly converted into a gelatinous mass, insoluble in alcohol, ether, and oil of turpentine, and no longer volatile without decomposition. Simon calls this *Oxide of Styrole.* It does not yield with nitric acid the same products as the styrole itself.

This oil is evidently a remarkable compound; and, as it differs in composition from all the other non-oxygenated oils, it merits a careful study.

Oil of Lemons, obtained by pressure from the peel of the fruit of *Citrus medica*, is generally yellowish, and slightly turbid. When purified by rectification, it is clear, colourless, has a strong and pleasant smell of lemons, and a hot pungent taste. It has a sp. g. of from 0·848 to 0·85 and higher, and boils from 330° to 353°, being a mixture of two oils which may be separated by distillation to a certain extent. The more volatile portion is also the lighter of the two. Reagents act on it very much as on oil of turpentine; and, like that oil, it forms with hydrochloric acid gas a solid and a liquid compound, which both have exactly the same composition, but contain for the same amount of carbon and hydrogen twice as much hydrochloric acid as the corresponding compounds of oil of turpentine. When deprived of the hydrochloric acid by quicklime, they yield two oils of the same composition: one of which, Citréne, has the sp. g. 0·847, and boils at 330°; the other, Citriléne, has the sp. g. 0·88, and boils at 345° to 353°. It is the former, Citréne, that yields the solid compound with hydrochloric acid. (Blanchet and Sell, Soubeiran and Capitaine, Dumas.)

Both oil of lemons and the two oils last described have the composition, in 100 parts, of oil of turpentine; and the formula $C_{10}H_8$, or more probably C_5H_4. The crystalline compound with hydrochloric acid seems to be $C_{10}H_9Cl$.

The oils of Cedro, and Cedrat, are probably identical, when pure, with oil of lemons.

Oil of Oranges, from orange peel, *Citrus aurantium*, differs only in smell from oil of lemons. Its composition and its actions with regeants are precisely the same.

Oil of Neroli, or of orange-flower, is quite distinct from the above oils, which are derived from the fruit. It has the peculiar fragrance of the flowers, and is in great part soluble in water; it is soon reddened by the action of air and light. Orange-flower water is a solution of this oil, obtained by distilling the flowers with water. Oil of neroli appears to contain a stearopténe, possibly a hydrate. The composition of the oil is not exactly known, and it is doubtful whether it contain oxygen or not.

Oil of Copaiva, obtained by distilling balsam of copaiva (from *Copaifera multijuga*) with water, is colourless, has the sp. g. 0·91, and boils at 473°. It is soluble in 2½ parts of absolute alcohol; but requires 25 to 30 parts of alcohol, sp. g. 0·85, for solution. Reagents act on it as on oil of turpentine. Nitric acid causes a kind of explosion; producing a crystalline compound, at first yellow, then blue, and finally becoming green. With hydrochloric acid it forms a crystalline compound, having the composition of that from oil of lemons, $C_{10}H_9Cl$; it also forms a liquid compound: but the radicals of these could not be isolated. (Soubeiran and Capitaine, Blanchet.) The oil of copaiva has the same composition as oil of turpentine. It is used in medicine.

Oil of Pepper, from *Piper nigrum*, has similar properties and the same composition; but it does not form a crystalline compound with hydrochloric acid, which it absorbs in large quantity.

Oil of Cubebs, from the fruit of *Piper cubeba*, is colourless and aromatic, sp. g. 0·929, boils at about 490°. It gives a crystalline compound with hydrochloric acid, which seems to be $C_{15}H_{13}Cl$. The oil is supposed by Soubeiran and Capitaine to be $C_{15}H_{12}$, which is still the same in 100 parts as oil of turpentine.

OXYGENATED ESSENTIAL OILS.

Oil of Bitter Almonds, obtained by distilling with water the bruised almonds after the fixed oil has been expressed, is yellow, and has a pleasant smell and a hot taste. It is a mixture of hyduret of benzule with hydrocyanic acid, both formed by the mutual action of amygdaline, emulsine or synaptase, and water. It is very poisonous. (See Benzule and its compounds.)

Oil of Laurel leaves, obtained by distilling the leaves of *Prunus* *laurocerasus* with water, appears to be essentially the same as oil of bitter almonds.

The leaves and kernels of the peach, *Amygdalus persica*, and of *Prunus padus*, as well as other species of Amygdalus and Prunus, yield a similar oil.

Oil of Spiræa. (See Salicule and its compounds.)

Oil of Cinnamon.—Of this oil there are two varieties; Ceylon oil of cinnamon, from *Laurus cinnamomum*, and common oil of cinnamon, from *Laurus cassia*. Both, when fresh, are pale yellow, but become brown on exposure to the air. They have a sweetish pungent aromatic taste, and a pleasant smell. Their sp. g. is from 1·03 to 1·09. (See Cinnamule and its compounds.) According to Mulder, both oils have the same composition, and the formula $C_{20}H_{11}O_2$, when quite fresh. On exposure to the air, they rapidly absorb oxygen; and produce cinnamic acid, two resins, and water. Mulder has analyzed both the resins, which he calls resin alpha and resin beta. The former is soluble in cold alcohol, and its formula is $C_{15}H_{7\frac{1}{2}}O_2$? The latter is insoluble in cold alcohol, and has the formula $C_{12}H_5O$. If we compare the composition of these resins and of cinnamic acid with that of the oil, we find that 3 at. of oil of cinnamon $= C_{60}H_{33}O_6 + 8$ at. oxygen $=$

$$C_{60}H_{33}O_{14} = \begin{cases} \text{1 at. cinnamic acid} & = C_{18}H_7\,O_3 \\ \text{1 at. resin beta} & = C_{12}H_5\,O \\ \text{2 at. resin alpha} & = C_{30}H_{15}O_4 \\ \text{6 at. water} & = \underline{\quad\; H_6\,O_6} \end{cases}$$

$$C_{60}H_{33}O_{14}.$$

The 8 atoms of oxygen are derived from the air. Oil of cinnamon is decomposed by hydrochloric acid gas; yielding a volatile oil not yet examined, water, and two resins, one soluble, the other insoluble, in cold alcohol. The formula of the latter is $C_{20}H_8O$; that of the former $C_{14}H_7O$. In like manner, concentrated sulphuric acid acts on the oil, producing two resins, one soluble, the other insoluble, in alcohol. The composition of the

$$\begin{array}{ll} \text{former is} \;\ldots\ldots & C_{30}H_{15}O_2 \text{ or} \\ \text{that of the latter} \;\ldots\ldots & \underline{C_{30}H_{15}O} \\ \text{Together} \;\ldots\ldots & C_{60}H_{30}O_3 \text{ which is} \end{array}$$

3 at. oil of cinnamon — 3 at. water. The sulphuric acid removes an atom of water from each atom of the oil, and the oxygen of the residue is unequally divided between the resins.

With nitric acid, oil of cinnamon forms a white crystalline compound, $C_{18}H_9NO_7$. The oil $C_{20}H_{11}O_2$ loses here C_2H_2, and takes up NO_5, and the rational formula of the resulting compound is probably $C_{18}H_8O_3 + NO_3 + HO$; which explains its decomposition by contact with water, and the formation of cinnamic acid when it is dissolved in sulphuric acid. With water it yields an oil which is $C_{18}H_8O_2$, that is, hyduret of cinnamule; while its solution in sulphuric acid, when mixed with water, deposits cinnamic acid, $C_{18}H_7O_3$.

Along with the crystalline compound, nitric acid produces a red oil, which is instantly decomposed by water, although not by anhydrous alcohol or ether. With water the red oil yields another oil, the formula of which is $C_{15}H_7O_2$. These results are taken from a very recent memoir by Mulder.

Oil of Cloves.—From the undeveloped buds of *Caryophyllus aromaticus.* Sp. g. 1·055. It is the least volatile of the essential oils, and is a mixture of caryophyllic acid and an indifferent or neutral oil. (See Caryophillic Acid.)

Oil of Sassafras. — From *Laurus Sassafras.* Sp. g. 1·08 to 1·09. It is coloured scarlet by nitric acid, yielding oxalic acid. When long kept, it deposits a stearopténe in large crystals, which melts in the heat of the hand, and is volatile.

Oil of Sweet Bay.—From *Laurus nobilis.* A dirty white, thick oil, with a pungent smell and a bitter taste. Sp. g. 0·914. By distillation it yields a lighter oil, sp. g. 0·857, and one less volatile, sp. 0·885, while a thick mass remains in the retort. The more volatile portion, according to Brandes, has the formula $C_{20}H_{16}O$, which is that of the oil of camphor.

Laurine is a crystalline substance which may be extracted from bay leaves by absolute alcohol. It is fusible and volatile, and seems to be a neutral substance.

Some other oils, little known, are derived from different species of Laurus and Persea, such as *Laurus Pichurim*, *Laurus Culilaban*, &c.

Oil of Saffron. —From the stigmata of *Crocus sativus.* It is yellow, heavier than water, and gradually changes into a white solid, lighter than water. It has the odour of saffron.

Oil of Bergamot.—This oil, from *Citrus Limetta* (the lime), and *Citrus Bergamotta* (the bergamot), has an odour resembling that of oil of lemons, from which, however, it differs in containing oxygen. It is believed to contain a mixture of oils, having the composition of citréne, with a hydrate of such an oil, and an oxygenated oil formed by the action of the atmosphere. It generally deposits a stearopténe, which Ohme calls Bergapténe; the formula of which, according to Ohme and Mulder, is C_3HO. According to Soubeiran and Capitaine, anhydrous phosphoric acid deprives the hydrate of its water, and the oil which separates has the composition of oil of lemons. A part of the oil seems to combine with phosphoric acid, producing an acid analogous to phosphovinic acid. With hydrochloric acid gas, oil of bergamot forms only a liquid compound.

Oil of Roses.—Otto or Attar of Roses, from the petals of *Rosa centifolia, moschata, sempervirens*, and other species. A yellowish thick oil, congealing in the cold to a buttery mass, composed of shining foliaceous crystals. When much diluted, its smell is highly agreeable; when strong, it causes headache. It has a mild aromatic taste, sp. g. 0·832. It consists of a solid (stearopténe), and a liquid oil, in variable proportions. The solid portion, which is insoluble in alcohol, and may be purified by solution in ether, has the formula CH, or some multiple of it.

Oil of Rhodium, from the wood of *Convolvulus scoparius*, has an odour of roses, and is sometimes used to adulterate oil of roses.

Oil of Rose Geranium, from *Pelargonium radula*, has also a similar odour, and is used for the same purpose; but it smells also of *Geranium Robertianum*. It is crystalline, and melts at 68°.

Oil of Cajeput, from *Melaleuca Leucodendron*, and *Melaleuca Cajeputi*. It has commonly a pale green colour. Its odour is unpleasant, except when much diluted, when it resembles that of camphor and rosemary; sp. g. 0·978. The green colour is natural to the oil, but is sometimes increased by the presence of copper, derived from the vessels in which it is kept. Blanchet and Sell found the composition of a very pure specimen to be $C_{10}H_9O$.

The *Oils of Nutmeg* and *Mace*, the former from the nut of *Myristica moschata*, the latter from the rind of the same nut, appear to be identical. They contain a liquid oil and a stearopténe. The latter, according to Mulder, is $C_8H_{16}O_3$.

Oil of Cardamom, from *Amomum repens*, belongs to this class of oils, but has not been minutely studied. It is aromatic, and its sp. g. is 0·945.

The *Stearopténe of the Tonka bean*, the fruit of *Dipterix odorata*, has a pleasant aromatic odour, is heavier than water, soluble in alcohol and ether.

Oil of Anise, from *Pimpinella anisum*, is solid at temperatures below 50°, owing to the crystallization of a stearopténe which it contains in large quantity. The solid portion, according to Cahours, has the formula $C_{22}H_{13}O_2$. With chlorine it forms a liquid compound, $C_{22}H_{10}Cl_3O_2$; with diluted nitric acid it yields a new acid, the compound of which with oxide of silver is $C_{16}H_6O_5$, AgO; and with fuming nitric acid another, the silver salt of which is $C_{16}H_5(NO_4)O_5$,AgO. Fused with hydrate of potash, it yields an acid, not further investigated. It also forms with sulphuric acid a solid compound; and with fuming sulphuric acid another new acid, which yields a soluble salt with baryta.

Oil of Dill, from *Anethum* or *Apium graveolens*, has the strong smell of the plant, and a sweetish burning taste; sp. g. 0·881.

Oil of Fennel, from *Anethum fœniculum*, has the odour of fennel, and the sp. g. 0·997. It contains a stearopténe, which seems to be the same as that of oil of anise. The difference between the two oils depends on the liquid portion.

The *Oil of Water Fennel*, from *Phellandrius aquaticus*, appears to contain ammonia, and is poisonous.

Oil of Parsley, from *Apium petroselinum*, has a strong smell of parsley, and contains a liquid and a solid portion. The former appears to have the composition of oil of turpentine; the latter is said by Loewig and Weidmann to be $C_{12}H_8O_3$.

Oil of Carraway, from *Carum carui*, appears to contain two oils differing in volatility. The more volatile seems to contain no oxygen; the other appears to be analogous to *oil of cumine.* (See Cuminic Acid.) The latter is derived from *Cuminum cyminum.*

Oil of Coriander, from *Coriandrum sativum*, has the smell of the seeds, and the very low sp. g. of 0·759.

Oil of Pimpernel, from *Pimpinella saxifraga*, has a golden yellow colour, an unpleasant smell of parsley, and is lighter than water. That from *P. magna* is at first blue, then green.

Oil of Peppermint, from *Mentha piperita*, has commonly a pale yellow or green colour, and a pungent cooling taste. Its sp. g. is 0·902 to 0·91. The American oil contains a stearopténe, which appears to be $C_{10}H_{10}O$. (Dumas, Blanchet and Sell.) According to Walter, this should be doubled, $C_{20}H_{20}O_2$; and by the action of anhydrous phosphoric or sulphuric acid 2 at. of water are removed, and a carbo-hydrogen is left $= C_{20}H_{18}$, which Walter calls Menthene: so that the rational formula of the stearopténe is $C_{20}H_{18}$, 2HO, or possibly $C_{20}H_{19}O,HO$. Treated with chloride of phosphorus, the stearoptène yields chloride of menthene $= C_{20}H_{17}Cl$. Chlorine gas produces two other compounds containing chlorine.

By the action of nitric acid, menthene yields a compound, $C_{10}H_9O_9$; and by the action of chlorine it is converted into another compound, $C_{20}H_{13}O_5$. (Walter.)

Oil of Pennyroyal, from *Mentha pulegium*, has, according to Kane, the formula $C_{10}H_8O$; which is remarkable, as being identical with that of camphor.

The *Oil of Mentha viridis*, according to Kane, is $C_{35}H_{28}O$.

Oil of Marjoram, from *Origanum majorana*, contains a stearoptène, which, according to Mulder, is $C_{14}H_{15}O_5$. The oils of Origanum Smyrnæum and of Origanum vulgare are similar, and are used to adulterate the oil of marjoram. According to Kane, the latter is $C_{50}H_{40}O$.

Oil of Lavender, from *Lavandula spica*, has the odour of the plant, the sp. g. 0·872, and boils at 365°. It contains a variable quantity of stearoptène, which, according to Dumas, is camphor.

Oil of Rosemary, from *Rosmarinus officinalis*, according to Kane is $C_{40}H_{36} + 2HO$. Sulphuric acid blackens it, and causes the separation of an oil, having an alliaceous smell, and the composition of oil of turpentine. Kane calls this oil Rosmarine.

Oil of Basil, from *Ocimum basilicum*, contains a stearoptène, which Dumas and Péligot found to be $C_{20}H_{16} + 6HO$, agreeing in composition with the hydrate of oil of turpentine. The liquid portion has not been examined.

Oil of Thyme, from *Thymus vulgaris*, has the odour of the plant, and deposits a stearoptène when kept.

Oil of Valerian, from *Valeriana officinalis*, contains valerianic acid (see that acid) and a stearoptène.

Oil of Rue, from *Ruta graveolens*, is yellow or greenish, has the sp. g. 0·837, and boils at a temperature from 425° to 473°. According to Will, its composition is $C_{28}H_{28}O_3$, and the density of its vapour, $= 7·69$, agrees with this formula.

Oil of Cascarilla, from the bark of *Croton eleutherium*, is sometimes yellow, at other times blue or green; has the sp. g. 0·938; and contains two oils, one boiling at 344°, the other less volatile. According to Völckel, the former contains no oxygen, and has probably the usual composition of non-oxygenated essential oils. The latter contains oxygen.

Oil of Chamomile, from *Matricaria chamomilla*, is dark blue, viscid, and has a bitter aromatic taste; sp. g. 0·924. Nitric acid decomposes it, and the addition of water to the acid solution precipitates a resin having the odour of musk. It dissolves iodine without producing heat, unless when adulterated with oil of turpentine or of lemons, when the violent action of iodine on these oils discovers the adulteration. The Roman oil of chamomile, from *Anthemis nobilis*, is very similar to the above.

Oil of Wormwood, from *Artemisia absinthium*, is greenish yellow, has an unpleasant bitter taste, and the sp. g. 0·897.

Oil of Tea, from *Thea viridis*, is yellow, and readily solidified by cold. It has the odour of tea in so high a degree that it is apt to cause stupefaction when smelt. In the process of drying the tea leaves, the greater part of the oil is lost, so that the best Hysoǹ yields hardly 1 p. c. of the oil.

The following vegetables yield oxygenated essential oils, of which however so little is known, that for the present we merely give the catalogue of the names. Many of them contain stearopténe or solid volatile oils.

Teucrium marum, Hyssopus officinalis, Salvia officinalis, Lycopus europæus, Ledum palustre, Achillea millefolium, Artemisia contra, Artemisia dracunculus, Artemisia vulgaris, Tanacetum vulgare, Juniperus lycia and thurifera, Balsamodendron myrrha, Galbanum officinale, Ferula persica, Cupressus sempervirens, Thuja occidentalis, Aristolochia serpentaria, Cæsalpina crista, Hedwigia balsamifera, Betula alba, Wintera aromatica, Populus nigra, Chenopodium ambrosioides, Dahlia pinnata, Parmelia parietina, Tilia europæa, Sambucus nigra, Reseda odorata, Philadelphus coronarius, Jasminum officinale, Syringa vulgaris, Convallaria majalis, Diosma crenata, Myrica gale, and others.

ESSENTIAL OILS CONTAINING SULPHUR.

Several essential oils contain sulphur; and, like all organic compounds in which sulphur is present in any form but that of its compounds with oxygen, they have generally a fetid smell.

Oil of Mustard is obtained from the seeds of *Sinapis nigra*, exactly as oil of bitter almonds from that fruit. The seeds, deprived of fixed oil by pressure, are made into a paste with water, and this after some hours is distilled. The oil is not ready formed in the seed, but is produced by the mutual action of substances contained in them along with water.

Oil of mustard has the sp. g. 1·038, is very pungent to the taste and smell. It contains sulphur and nitrogen, formula $C_8H_5NS_2$; when heated with potash it yields ammonia, sulphuret of potassium, and sulphocyanide of potassium. With ammonia it yields a white crystalline compound, which appears to be composed of $C_8H_8N_2S_2$, or $C_8H_5NS_2 + NH_3$. The nature of this curious compound is still doubtful.

Both black and white mustard, according to Bussy, contain a substance analogous to emulsine or synaptase, called by him Myrosine; and an acid, Myronic acid, which, by the contact of myrosine and water, yields the oil of mustard with other products not yet investigated. Myronic acid occurs in the seeds combined with potash, and the myronate of potash is the substance described by Henry and Garot as Sulphosinapine. It is remarkable that white mustard, although containing myrosine, which is identical with that of black mustard, and apparently also myronic acid, does not yield with water the oil of mustard, but another pungent oil. But the myrosine of white mustard, when added to the residue of black mustard deprived of its myrosine, yields the oil, just as the emulsine of sweet almonds acts on the amygdaline of bitter almonds.

By the action of hydrated oxide of lead, with the aid of a gentle heat, oil of mustard is deprived of all its sulphur; the mixture, distilled with water, yields an ammoniacal liquid, and along with the sulphuret of lead there is found a crystalline substance, called by Simon *Sinapoline.* Its formula appears to be $C_{28}H_{24}N_4O_4$.

It is obvious that the white mustard must contain a substance differing from myronic acid, else it would yield the same oil as black mustard; but this point is still very obscure, and Bussy has not yet published his analysis of myronic acid, which contains carbon, hydrogen, nitrogen, oxygen, and sulphur. It forms salts which have a bitter taste, and no smell. These salts, as well as the acid itself, when distilled with myrosine and water, yield the volatile oil. Some of them are crystallisable.

Besides myronic acid, and myrosine, black mustard may be made to yield a neutral crystalline body, discovered by Simon, who calls it Sinapisine. It is obtained by digesting the seeds in strong alcohol, and acting on the alcoholic extract with ether. Its properties resemble those of the unsaponifiable crystalline fats. If the seeds, after the action of the alcohol, be digested with carbonate of soda, and the solution distilled with an excess of sulphuric acid, there is obtained a volatile acid, not unlike acetic or formic acid. Its salts are extremely soluble, and difficultly crystallizable. Both these compounds require a minute investigation, and the same may be said of the whole subject of the mustard-seed and its volatile oil.

Oil of Horseradish, from *Cochlearia armoracia* and *C. officinalis*, has a very pungent taste and strong smell. It contains sulphur, and causes blisters when applied to the skin.

Oil of Garlic, from *Allium sativum*, has the smell of the plant, and smarts the skin when applied to it.

The onion, *Allium cepa*, yields a similar oil.

Oil of Assafetida, from *Ferula assafetida*, has a still more offensive smell, and a taste at first mild, afterwards acrid. When rubbed with mercury it forms sulphuret of mercury.

The oils of water-pepper, *Polygonum hydropiper* and of *Arum maculatum*, also belong to this class; as do those of *Lepidium latifolium*, and of hops, *Humulus lupulus*.

APPENDIX TO THE ESSENTIAL OILS.

It is proper to mention here several substances which resemble the stearopténes in so far as they are volatile, with few exceptions crystalline, and may be distilled along with the vapour of water.

Helenine, from *Inula Helenium*, may be obtained by acting on the fresh root with hot alcohol, or by distilling it with water. It crystallizes in white prisms, soluble in alcohol, ether, and essential oils, but insoluble in water. It melts at 162°, and boils about 530°. According to Dumas, its formula is $C_{14}H_9O_2$; according to Gerhardt, it is $C_{15}H_{10}O_2$. When helenine is heated with nitric acid till the product is entirely soluble in ammonia, and the solution mixed with water, there is precipitated a peculiar substance, nitro-helenine, which appears to be $C_{15}H_9O_2 + NO_4$. (Gerhardt.) With chlorine it yields chloride of helenine, $C_{15}H_{10}O_2 + Cl_2$; and Gerhardt obtained another substance, apparently a compound of this last with hydrochloric acid. Both are yellow powders. The latter, heated with quicklime, yields naphthaline. With anhydrous phosphoric acid, helenine yields a carbo-hydrogen, helenéne, $= C_{15}H_8$, which is helenine — 2 at. water. With sulphuric acid, helenine forms a new acid, which, on account of its easy spontaneous decomposition, could not be examined.

Asarine, obtained by distilling the root of *Asarum Europæum* with water, is a crystallized solid, with an aromatic taste and smell like those of camphor, fusible in boiling water, and softened by the heat of the hand. Its sp. g. is 0·95. It sublimes unchanged when heated to about 570°. Its formula, according to Blanchet and Sell, is $C_{16}H_{11}O_4$; and these chemists consider it as the hydrate of an oil contained in the root, which they extracted by means of absolute alcohol. Their analysis of the oil, however, does not agree with this view.

Nicotianine is a fatty substance, obtained in minute quantity by distilling tobacco leaves with water. It is insoluble in water; soluble in alcohol, ether, and potash. It has a bitter taste, and a strong smell of tobacco.

Anemonine occurs in *Anemone pulsatilla*, *nemorosa*, and *pratensis*. It is crystalline, heavier than water, and, when heated in a current of air, sublimes with a pungent acrid smell, but cannot be distilled unchanged in close vessels. According to Löwig, its formula is $C_7H_3O_4$. He found it soluble in ether. But Fehling states that it is very sparingly soluble in that menstruum, and soluble in hot alcohol. Four analyses by Fehling give the formula $C_5H_2O_2$. By boiling it with oxide of lead and water he obtained a compound which seems to be $C_{15}H_6O_6,PbO$. By the action of baryta Löwig obtained an acid, Anemonic acid, the formula of which he states to be $C_7H_4O_3,HO$.

The pods of *Epidendron Vanilla* yield a crystalline body in soft needles, and the wood of *Quassia amara* also contains a crystalline body. Neither of these has been much studied. The seeds of *Tanghinia Madagascariensis* yield to ether a crystalline substance, which is highly poisonous.

According to Bonastre, Massoy bark contains a camphor-like substance, along with two volatile oils.

Hünefeldt has shown that the root of *Primula auricula* contains a volatile crystalline body, which has an odour resembling that of peppermint; and that the root of Primula veris yields another, which smells like fennel and garlic. He calls them Auricula camphor and Primrose camphor.

Cantharidine is a volatile crystalline body, contained in the insects Lytta ruficollis, L. gigas, and L. vittata. It is very soluble in ether, alcohol, and essential oils, and is volatile. It is the source of the blistering power of the insects. Regnault found it to be composed of $C_{10}H_6O_4$.

CAOUTCHOUC.

This remarkable substance, which has some analogy with the resins, occurs in the form of bottles, which are made by allowing the juice of the trees which yield it to flow from incisions on shapes of unburnt clay, which are broken when the caoutchouc has attained a sufficient thickness.

Caoutchouc is obtained from several trees, both in Asia and America, and particularly from *Siphonia elastica*, *Tabernæmontana elastica*, and *Lobelia caoutchouc*. The former has been variously named, and is known as *Jatropha elastica*, *Hevea Guianensis*, *Siphonia cahuchu*. The second named plant, *Tabernæmontana* has also been named *Urceola elastica*. Several species of *Ficus*, and many other plants, contain it likewise.

The juice is sometimes imported in closely stopped vessels. It is yellowish and thick, like cream; and has a sour smell, arising from the putrefaction of the vegetable albumen it contains. This albumen is coagulated by heat, and thereby causes the separation of the suspended caoutchouc. According to Faraday, the juice contains, in 100 parts, 32 of caoutchouc, 2 of vegetable albumen, 7 of a nitrogenised substance soluble in water, 3 of a substance insoluble in water, and 56 of water.

Pure caoutchouc is transparent and colourless, the black colour of the commercial article being derived from the smoke in which it is dried. It is perfectly elastic, and, when suddenly stretched, gives out much heat and free electricity. It is a nonconductor of electricity. When it has once separated from the juice in the solid form, there is no method known of obtaining it again suspended as before. In hot water it swells and becomes soft, but is utterly insoluble both in water and alcohol. Pure ether dissolves it, and leaves it by evaporation in a perfectly elastic state, and with a surface like that obtained by cutting it, when it has the property of adhering firmly to another similar surface if the two be strongly pressed together. This property enables us to form tubes from a plate of caoutchouc by folding it round a cylinder, cutting off the superfluous edges with a clean and sharp pair of scissors, and then pressing together the fresh cut edges. Tubes thus made are perfectly air and water tight. In rectified naphtha from wood or coal tar, caoutchouc is soluble; and the water-proof cloth of Mackintosh is made with a viscid solution in a mixture of oil of turpentine and coal naphtha, the solvent being removed by evaporation in chambers heated by steam, and leaving the caoutchouc with all its properties. Essential oils will also dissolve it alone; but from the presence in them of resin, which remains after evaporation of the oil, the caoutchouc does not dry properly, but remains viscid.

Heated to 248° it melts, and continues long viscid and soft. In this state it may be used as a luting, where a high temperature is not employed.

When more strongly heated, it is decomposed, and the greater part distils over in the form of a mixture of oily liquids. These differ extremely in volatility; the most volatile portion boiling about 90°, the least volatile at 680°, and the greater portion at intermediate temperatures. According to Himly, all these oils have the empirical formula C_5H_4, which is that of oil of turpentine. Gregory found a portion which boiled at 97° to have very nearly the composition of olefiant gas, C_2H_2; and, when this oil was acted on by sulphuric acid, it blackened, gave off sulphurous acid, and, on the addition of water, yielded an oil which boiled at a temperature above 428°, but still having the same composition.

By careful rectification Himly obtained an oil, the boiling point of which was constant at 339°, which he calls Caoutchine. It had the composition of oil of turpentine. Bouchardat, by applying intense cold to the receiver, obtained a liquid, Caoutchéne, which boiled below 32°, and is probably identical with Faraday's quadricarburetted hydrogen, C_4H_4. He also analysed another oil, Heveéne, boiling at 599°, which had the same composition. From the experiments of Himly, Bouchardat, and Gregory, therefore, it appears that caoutchouc by distillation yields many oily liquids, some of which have the composition of olefiant gas, and others that of oil of turpentine. The most volatile liquid above mentioned had the very low sp. g. of 0·654. Himly's caoutchine had the sp. g. 0·842.

The purest caoutchouc that Faraday could obtain from the juice was found by him to contain 87·2 p. c. of carbon, and 12·8 p. c. hydrogen.

RESINS.

This class of compounds occurs almost exclusively among vegetables. They either flow from them dissolved in essential oils, forming balsams, or are found deposited in the wood. What are called fossil resins are doubtless derived from extinct vegetation.

There is a close connection between resins and the oils in which they occur dissolved. All resins contain oxygen, and most essential oils become resinous by the absorption of oxygen from the air. It is not, however, probable, that resins are merely the oxides of essential oils. From the fact that iodine, a substance which has a very feeble attraction for hydrogen, acts strongly on essential oils, depriving them of a part of their hydrogen, it is obvious that that portion of hydrogen is in a different state of combination from the remainder; and it is most probable that the oxygen of the air removes this loosely combined hydrogen, forming water, while oxygen also replaces the hydrogen which has been removed. The water thus formed may either remain in combination with the new oxidised compound, or be separated.

Hence, when an essential oil is converted into resin by exposure to the air, the composition of the resin must be equal to that of the oil, *minus* a certain quantity of hydrogen, and *plus* a certain quantity of oxygen.

This appears to be the relation between common resin and oil of turpentine, and between the resin and oil of copaiva. Both of the oils are C_5H_4 or $C_{10}H_8$; and the resins are $C_{10}H_7O$, or, if we adopt the atomic weights as found by Rose, $C_{40}H_{28}O_4$. Here $C_{40}H_{32}$ have lost 4 eq. hydrogen, and gained 4 eq. oxygen. But the best analyses of these resins agree even better with the formula $C_{40}H_{30}O_4$. If this last be the correct formula, $C_{40}H_{32}$ have lost 2 eq. of hydrogen, replaced by 2 eq. oxygen, yielding the oxide $C_{40}H_{30}O_2$; and this oxide has then combined with 2 eq. oxygen, giving the rational formula $C_{40}H_{30}O_2 + O_2$.

If from this we reason backwards to the constitution of oil of turpentine, it will appear that that oil is $C_{40}H_{30} + H_2$ or $C_{20}H_{15} + H$, in which formulæ part of the hydrogen belongs to the radical, and the remainder is removable and replaceable by other elements, such as oxygen, iodine, or chlorine. This would also account for the tendency of oil of turpentine, as the hyduret of a compound radical, to unite with hydrochloric acid, the hyduret of a simple radical; just as ammonia, the hyduret of amide, or olefiant gas, the hyduret of acetule, unite with the same acid.

From the balsams, which, as already mentioned, are mixtures of resins with essential oils, the former are obtained pure by distillation with water, as long as any oil passes over.

There are distinguished hard and soft resins. The hard resins are brittle, colourless when pure, although often tinged yellow or brown by foreign matters. They are heavier than water, and non-conductors of electricity. When warmed, they have a slight odour, probably arising from traces of oil. Those which are insoluble in water are tasteless; many, which are sparingly soluble, have a bitter taste. They soften in boiling water, but generally require a higher temperature to melt them. They are decomposed by a strong heat, yielding combustible gases and volatile combustible liquids, with a residue of porous charcoal. They are easily inflammable, and burn with a smoky flame. When acted on by nitric acid, the resins yield oxalic acid, and a series of products not yet examined.

The resins occurring in nature are generally mixtures of several, differing in their characters. Some are exceedingly soluble in cold alcohol; while others are dissolved with difficulty, even by boiling alcohol. Several resins may be obtained in crystals from their alcoholic solutions; and the addition of water to all such solutions precipitates the resin, giving the mixture a milky aspect.

Many resins are soluble, others insoluble, in ether. They dissolve in fixed and essential oils, and also in sulphuret of carbon. The action of alkalies distinguishes one class of resins from another. A certain number, when dissolved, redden litmus, combine with bases, and possess all the characters of acids. Others are neutral, and do not combine with bases.

The most decidedly acid resins decompose the carbonated alkalies with the aid of heat, and readily dissolve in caustic alkalies. Their solution in alcohol is not precipitated by ammonia, and the precipitate caused by water is entirely soluble in ammonia. The alcoholic solution of the neutral resins is precipitated by ammonia.

The acid resins when dissolved in ammonia cause a crystalline precipitate in nitrate of silver, which is insoluble in excess of ammonia. The neutral resins cause no such precipitate.

The compounds of the acid resins with alkalies are called resinous soaps; but they cannot, like true soaps, be separated from their solutions by common salt, and when concentrated they do not form mucilaginous or gelatinous solutions, as soaps do. These solutions, however, froth when agitated, like a solution of soap. Some of these resinous soaps are insoluble in caustic potash, others soluble.

Common Resin, or ***Rosin***, is obtained from the turpentine or balsam of Pinus sylvestris, pinaster, abies, and picea, by distillation with water till all the oil is removed. It is also named Colophon or Colophonium. It is nearly white when pure, (Resina alba,) but is commonly yellow or brown. It is a mixture of three acid resins, Sylvic, Pinic, and Colopholic acids.

Sylvic Acid is extracted from the resin by weak alcohol, and purified by stronger alcohol. It crystallizes in minute prisms, which lose no weight when heated to 212°. With alkalies it forms salts which are soluble in ether and alcohol.

Formula, $C_{20}H_{15}O_2$ (Trommsdorff), or $C_{20}H_{16}O_2$ (Rose).

Pinic Acid is left undissolved by alcohol of 72 p. c. It is purified by combining it with oxide of copper, which is done by adding acetate of copper to its solution in strong alcohol. The pinate of copper is decomposed by hydrochloric acid, and the pinic acid repeatedly boiled with water. It does not crystallize, but in other respects is analogous to sylvic acid. Its formula is $C_{20}H_{15}O_2$ (Liebig).

Colopholic Acid is produced by distilling pinic acid, and has a brown colour, but the same composition, and a stronger affinity for bases. When colophon has been strongly heated, part of the pinic acid is always converted into colopholic acid, so that it is present in that substance in variable quantity.

In the turpentine of *Pinus maritima* Laurent has discovered another acid, *Pimaric acid*, which is isomeric with the preceding acids, and which crystallizes from hot alcohol. By distillation in vacuo it yields another isomeric modification, *Pyromaric acid;* and, by the action of nitric acid, a third acid, *Azomaric acid*, the formula of which is $C_{20}H_{11}NO_8$. When pimaric acid is distilled under the ordinary pressure, it yields a neutral substance, *Pimarone*, which contains 1 at. of water less.

Fremy, by distilling resin with lime obtained two oils, Resinone and Resinéone; the former of which is $C_{10}H_9O$, the latter $C_{29}H_{23}O$.

When common resin is repeatedly heated with water to dryness, it yields what is called pitch, shoemaker's rosin, or Burgundy pitch. A still stronger heat produces the black pitch used for naval purposes. When distilled, resin yields a large quantity of gas of good quality for illumination.

The *Resin of Copaiva Balsam*, when purified from the essential oil, is a crystallizable acid resin, and has the same composition in 100 parts as Colophon or Camphor. According to Rose, its formula, deduced from its salts, is $C_{40}H_{32}O_4$.

The *Resin of Elemi* contains two, one of which is crystallizable, but both are neutral. Their composition is the same as that of the resins already described. The resin called Gum Animé, from *Hymenæa Courbaril*, likewise contains two resins, which seem to have acid properties. The resin of Euphorbium seems to be identical in composition and in most of its properties with that of Elemi.

Gum Benzoin, the inspissated juice of *Styrax Benzoin*, contains, besides benzoic acid and an essential oil, three resins, namely, resins alpha, beta, and gamma. The latter is acid, the two former neutral. According to Van der Vliet, their composition is as follows:

Resin Alpha $= C_{70}H_{42}O_{14}$
—— Beta $= C_{40}H_{22}O_9$
—— Gamma $= C_{30}H_{20}O_5$

It is obvious that resin alpha contains the elements of the other two; and in fact, if the original mixture be long enough boiled with carbonate of potash, the resin alpha disappears, while gamma is dissolved, and beta left.

Styracine.—The balsams of Mecca and Peru, and storax, contain resin, essential oil, and, in the two latter, benzoic and cinnamic acids. The resins have been little examined; but Simon has extracted from storax a crystalline substance, which he calls Styracine. It is neutral, and has the properties of a resin. Its formula is $C_{24}H_{11}O_2$. Distilled with nitric acid, it yields hydrate of benzule, hydrocyanic acid, and other products. When distilled with hydrate of lime, it yields an oil, isomeric with benzine, but differing from it in properties; and, when distilled with aqua potassæ, it yields another oil, *Styraçone*, while the alkali is found combined with cinnamic acid, and mixed with a resinous matter. (Simon.)

Guaiacum, the resinous mass derived from *Guaiacum officinale*, contains a peculiar resin, distinguished by the property of striking a blue colour with many substances, such as mucilage of gum arabic, the roots of althæa, of cochlearia, of potatoe, of endive, of onions; also with nitrous acid, nitrous ether, and sweet spirit of nitre, as well as salts of iron and copper. The alcoholic tincture of guaiacum is the form in which this reaction is best observed. The guaiacum itself, by exposure to the air, becomes blue or green. It contains, besides more than one resin, not sufficiently studied, a bitter acrid substance, *Guaiacine*, the nature of which is uncertain. Guaiacum is used in medicine in the form of tincture, and in pills; and its compound with potash, called soap of guaiacum, is also employed.

Lac is obtained from punctures made by an insect in several species of Ficus, and also from Zicyphus jujuba. It occurs in three forms, stick, seed, and shell lac; the latter being the purest. It contains several resins, along with a peculiar colouring matter. It is an ingredient in the better kinds of sealing wax, and is much used for varnishes.

Mastic, from *Pistacia lentiscus*, and *Sandarac*, from *Juniperus communis*, grown in tropical regions, are two fragrant resins, containing each two or three different resins, and are also much used in making varnishes.

Copal, said formerly to have been derived from *Rhus copallanum*, seems by later accounts to be obtained from various species of *Hymenæa*, *Trachylobium*, and *Vouapa*. It has so much resemblance to amber, that it might be supposed to have a fossil origin; and, at all events, it has probably been long exposed to the action of the air before it has been collected. It is, of all resins, that which makes the finest varnishes, but it is at the same time the most difficult to dissolve. It may be dissolved in absolute alcohol, by first acting on it with aqua ammoniæ, which softens it into a gelatinous mass, and then adding the alcohol in small portions, with the aid of heat. It may likewise be dissolved in alcohol after being softened with ether. It is somewhat soluble in oil of rosemary, less so in oil of turpentine. But the common copal varnish is made by melting it cautiously, and adding oil of turpentine, heated to a certain point. According to Unverdorben, copal contains not less than five different resins, with a trace of essential oil.

The resin called *Dammar*, lately introduced, is derived from some unknown tree. It resembles copal, and makes excellent varnish.

Other resins, of whose chemical characters little is known, are Dragon's blood, from *Dracena Draco*, Takamahaka, Ladanum, the resin of Jalap, the root of *Convolvolus Jalappa*, that of Scammony, from *C. scammonium*, that of castor, that of birch bark, &c.

The following plants likewise contain resinous substances; *Iris florentina*, *Piper nigrum*, *Capsicum annuum*, *Pimpinella saxifraga*, *Helleborus hyemalis*, *Arnica montana*, *Anthemis pyrethrum*, *&c.*

RESINOUS VARNISHES.

These varnishes are made by dissolving resins in strong alcohol, or oil of turpentine. The resins principally used for varnishes are mastic, sandarach, shell lac, elemi, and copal. To dissolve the latter, it is melted, mixed while hot with a little drying oil, and to the mixture oil of turpentine, in quantity equal to the resin, is added by small portions. Spirit varnishes are more brittle, those with oil of turpentine more plastic, as the oil itself in drying yields a soft resin.

PRODUCTS OF THE DISTILLATION OF COMMON RESIN.

When resin is subjected to heat in close vessels, it yields a large quantity of gaseous carbo-hydrogens, and several liquids, also composed of carbon and hydrogen. The subject has been investigated by Frémy, and by Pelletier and Walter.

Frémy states, that, when distilled at the lowest possible temperature, resin yields, besides water and other products, an oily liquid, Resineine, the formula of which is $C_{20}H_{15}O$.

When distilled at a higher temperature, there is obtained, according to Pelletier and Walter, a liquid, Retinaphtha, the formula of which is C_7H_4. Treated with chlorine, retinaphtha yields a compound, $C_{14}H_6Cl_2$; and a similar compound may be formed with bromine. Along with retinaphtha there is formed another liquid, less volatile, Retinule, the formula of which is C_9H_6; and in the more fixed and oily product of the distillation of resin there are found a liquid, Retinole, the formula of which is C_8H_4, and a solid compound, in appearance like a crystalline fat, which is called Metanaphthaline or Retistérene, and which has the composition of naphthaline.

NON-AZOTIZED VEGETABLE COLOURING MATTERS.

The varied colours of vegetables are owing to the presence of certain definite chemical compounds, which are called colouring matters. They are very numerous, and two or more are commonly found together. It is consequently difficult to obtain them in a state of purity, and hence their chemical characters are but imperfectly known.

Many of them are soluble in water; some only in alcohol or ether. They are all capable of combining with alkalies, and many of them combine also with acids. When exposed to light, especially if moist, they are bleached, absorbing oxygen at the same time; and their tendency to absorb oxygen is much augmented when they are dissolved in alkaline fluids.

The colour of these substances is generally changed by the action both of acids and alkalies: the latter change the yellow to brown, the red to violet, blue, or green; while the former change the blue to red, and the red to a brighter tint.

Many of these colouring matters are not found in the living or fresh plant with the properties which they exhibit when separated by chemical means. Thus madder-root, when fresh, is yellow, and becomes red only after undergoing a species of fermentation; fresh logwood is brownish yellow, and becomes red by exposure to the air. In such cases, the colouring matter is formed by absorption of oxygen; and, when this is removed by deoxidising agents, the colour is destroyed, but is often restored on exposure to the atmosphere.

Some colourless substances, such as gallic and tannic acids, when dissolved in an alkali, rapidly absorb oxygen and give rise to dark blue or purple colouring matters.

Another class of colourless substances, which absorb oxygen when in contact with ammonia, give rise to very fine colouring matters. In this way are produced indigo, litmus, orceine, phloridzeine, &c. As these colouring matters, however, contain nitrogen, we shall describe them in a separate section.

All vegetable colouring matters are destroyed by chlorine, and cannot afterwards be restored. Most of them are bleached by sulphurous acid; but, on the addition of a stronger acid, the colour reappears, modified by the action of the acid employed.

The tendency of these colouring matters to combine with alumina is very powerful. They also combine readily with peroxide of tin, and with other similar oxides, which are, as it were, intermediate between acids and alkalies. The compounds thus formed are insoluble in water, and may be used in painting. They are called *lakes.*

Alumina, and the other oxides above alluded to, are also employed to attach the colouring matters to cloth, for the fibre of which these oxides have also a strong attraction.

The number of colouring matters is so great, and their chemical relations and composition are so little known, that we can only give a list of the more important.

1. YELLOW COLOURING MATTERS.

Turmeric yellow, or *Curcumine*, from the root of *Curcuma longa.*—It is extracted by alcohol, has a resinous aspect, and, when powdered, a bright yellow colour. It is turned brown by alkalies, and is used as a test of alkalinity.

Gamboge yellow is extracted by ether from gamboge, the inspissated juice of *Garcinia gambogia*, or *Stalagmites gambogioides.* It is resinous, and acts as a drastic purgative. It amounts to from 60 to 90 per cent. of gamboge.

Annotto is obtained by kneading with water the seeds of *Bixa orellana* or *Metella tinctoria.* According to Chevreul, it contains two colouring matters, a yellow and a red.

Carotine is the colouring matter of the carrot, *Daucus carota.* It is extracted by ether, and crystallises in small ruby-red crystals, which are soluble in fixed oils.

Rhabarberine or *Rheine* is found along with tannin in the different varieties of rhubarb. It is soluble in alcohol, crystalline, and of an orange colour. It dissolves in alkalies, with a violet colour; and from this solution alum throws down a fine red lake. It is fusible, and may be volatilised without decomposition.

Rhaponticine, analogous to the preceding, is found in *Rheum rhaponticum.*

Woad yellow, or *Luteoline*, is found in every part of woad, *Reseda luteola.* It is volatile and crystallisable.

Quercitron yellow, or *Quercitrine*, is the colouring matter of the bark of Quercus nigra (*Q. tinctoria*, Mich.) According to

Bolley, it is a yellow powder, partly crystalline, the formula of which is $C_{16}H_8O_9 + HO$. By adding to its solution in alcohol an alcoholic solution of acetate of lead, Bolley obtained a yellow salt, which he found to be $C_{16}H_8O_9$, PbO. He calls it *Quercitric Acid.*

Morine, obtained by Chevreul from the wood of *Brousonettia* or *Morus tinctoria.* Yellow bitter needles, soluble in alcohol and ether. When distilled, it is partly decomposed, yielding a yellow liquid, which on cooling solidifies into reddish orange crystals. A similar substance is obtained from *Rhus cotinus.*

Safflower yellow is extracted by water from *Carthamus tinctorius.* It is not yet known in a state of purity.

Saffron yellow, or *Polychroite*, is the chief ingredient in the petals of *Crocus sativus* (saffron). It has not been produced in a state of purity.

Similar yellow colouring matters, often crystalline, are obtained from the flowers of *Datisca cannabina*, *Spiræa ulmaria*, *Narcissus pseudo-narcissus ;* also from *Lichen parietinus*, from *nutgalls*, from *Chelidonium majus*, *Genista tinctoria*, *Serratula tinctoria*, *Betula alba*, *Rhamnus cathartica*, *R. infectoria*, and other plants.

Xanthophyll, or the *yellow of leaves*, is found in those leaves which become yellow in autumn. It is probably formed from *Chlorophyll*, the *green of leaves*, which, however, cannot be reproduced from it.

2. RED COLOURING MATTERS.

Dragon's blood, or, when pure, *Draconine*, is obtained from the gum-resin so called, which is produced by several species of *Calamus*, also by *Dracæna draco* and *Pterocarpus draco.* In mass it is reddish brown, in powder bright red. Dragon's blood is used in painting, dyeing, and varnishing.

Santaline is the red colouring matter extracted by alcohol from the wood of *Pterocarpus santalinus.* It has, like the preceding, a resinous aspect, and a dark red colour with frequent reflection of green. It is very soluble in alkalies; also in acetic acid, alcohol, and ether.

Anchusine, or *Anchusic Acid*, obtained from the root of *Anchusa tinctoria.* It yields a dark red fusible mass, which, if cautiously heated, yields violet-coloured vapours. It dissolves in alkalies with a blue colour, and is used as a test of alkalinity. It is properly the false alkanet. The true or oriental alkanet is obtained from Lawsonia inermis. (See Journal de Pharmacie, 1824; page 405.)

A similar resinous red colouring matter is obtained from the flowers and seeds of *Hypericum perforatum*, and from the leaves of *Bignonia chica*.

Safflower red or *Carthamine.*—It is extracted from *Carthamus tinctorius* (previously purified from the yellow matter by acetic acid) by a solution of carbonate of soda. When this is carefully neutralised by citric acid, carthamine is precipitated. It yields a dark red powder, reflecting a metallic green on the surface, but exhibiting a beautiful reddish purple in very thin layers. It has acid properties, and is used for dyeing rose-colour; also in painting, where it is often employed in the form of what are called pink saucers; and for rouge, under the name of *Rouge végétale*.

Madder.—This substance, the wood of the root of *Rubia tinctorum*, has been frequently examined. The latest experiments are those of Runge, who describes five colouring matters contained in it: three red, insoluble in water; one yellow, soluble in water; and one brown, which is insoluble.

The three red colouring matters are *madder purple*, *madder red*, and *madder orange*.

When the madder is washed with cold water and boiled with a strong solution of alum, the filtered liquid on cooling deposits a reddish brown substance, chiefly composed of *madder red*. When purified from the purple, it forms a crystalline brownish yellow powder. It is fusible, and sublimes in brilliant orange needles. It gives to alcohol and ether a reddish yellow colour, to acids a yellow, to ammonia a purple, and to potash or lime a violet tint. It is the substance which produces the so-called Turkey red dye.

The solution which has deposited the mass containing the *madder red*, when acidulated with sulphuric acid, deposits slowly a red precipitate, which contains the greater part of the *madder purple*. It dissolves, when pure, in alcohol, and is deposited in orange crystals. It is volatile, but does not yield a crystalline sublimate. Alkalies dissolve it with a bright red colour.

To obtain the *madder orange*, the roots, previously well washed, are digested with tepid water, and the liquid strained through muslin. On standing, it deposits the *madder orange* in glimmering scales, which are purified by solution in alcohol, from which they are deposited on cooling. It dissolves in ammonia with a reddish brown colour, in potash with a rose-red. It may be sublimed, and yields a yellow mass.

These three colouring matters, together or separately, give all the different tints obtained from madder. The *Alizarine* of Robiquet (from alizari, the name given to madder in the Levant) is chiefly madder red; but as it is obtained by sublimation, and as all three are volatile, it is necessarily mixed with the other two. They are all soluble in albumen, and have a tendency to combine with phosphate of lime. Hence, in animals fed with madder, the bones become red.

Madder yellow is obtained by acting on madder with water, and adding lime to the solution. The precipitate thus formed is dissolved in acetic acid, and the solution evaporated to dryness. Alcohol now dissolves the yellow matter, which is precipitated of a scarlet colour by acetate of lead. When this precipitate is decomposed by sulphuretted hydrogen, there is obtained a fine yellow solution of madder yellow.

Madder brown is insoluble in water or alcohol, soluble in alkalies. It cannot be used in dyeing.

It has been already mentioned that fresh madder-root is not red, but yellow; and that the red colour is formed by a species of fermentation, or rather decay, to which the oxygen of the atmosphere is essential. This change has not been properly studied; and it is not improbable that all the colouring matters of this dye stuff are products of the decomposition of one and the same original compound. They all yield, when carefully heated, a sublimate of orange crystals, called by Robiquet and Colin, who discovered them, Alizarine. These crystals may be made to yield all the tints of red obtained from madder; and, when fixed on cloth, colours thus obtained are as durable as those made in the ordinary way from the root.

When cotton cloth is treated with acetate of alumina, a portion of the earth attaches itself to the fibre; and, when the cloth is now boiled with madder, the colouring matter combines with the alumina, and is thus fixed on the cloth in tints of red, varying with the amount of madder employed. If acetate of iron be used, the tints obtained are purple.

The process for obtaining the Turkey red is very complicated, and is not yet sufficiently understood to enable us to explain the effect produced by the different means employed. There is little doubt that it will be found to admit of much simplification, when the subject shall have been properly investigated.

Alizarine.—To obtain this substance, madder red, however prepared, may be gently sublimed: or powdered madder may be cautiously charred by adding it gradually to its own weight of oil of vitriol, which decomposes everything except the alizarine. (Robiquet and Colin.) The carbonaceous mass is well washed with water, dried and gently heated, when it yields crystals of alizarine. These crystals have a fine orange-red colour. They dissolve sparingly in hot water and alcohol, to which they give a rose-red colour. They also dissolve in alkalies with a purple colour. Alizarine appears to stand in the same relation to the red of madder as sublimed indigo to common indigo. It has not yet been obtained in a state of perfect purity, so that its composition is not ascertained.

Madder lake, much prized as a pigment, is made by washing madder with cold water, boiling the residue with a solution of one part of alum in twelve of water, and precipitating the decoction gradually with carbonate of soda, or with borax. The precipitates first obtained are the most beautiful.

Hæmatoxylin.—This is the red colouring matter of logwood, *Hæmatoxylum Campechianum.* It is soluble in water, more so in alcohol, from which latter solvent it crystallises in shining orange crystals. It colours water red; acids brighten the colour, alkalies turn it to purple or blue. It is decolorised by sulphuretted hydrogen and other deoxidising agents, but becomes red again by exposure to the air.

With an alum mordant, logwood yields a violet dye; with iron, a black. It is used in dyeing black cloth and hats, which are hence reddened by acids.

Breziline is the red of Brazil wood (*Cæsalpina Braziliensis, C. crista?*) Soluble in water and alcohol; and crystallisable, according to Chevreul, who obtained small orange-coloured needles. Acids turn it yellow, alkalies violet. In the wood it is yellow, owing to the presence of acid, and the addition of alkalies developes the colour. It is a delicate test of alkalinity. With alum it yields a red dye, which is brilliant, but not durable.

A still finer but equally fugitive dye is obtained from *camwood*, a wood imported into England from Africa, the origin of which is unknown.

The red colouring matter of many flowers, such as *Rosa centifolia*, *Pæonia officinalis*, *Papaver rhœas*, *Althæa rosea*, *Dianthus caryophyllus*, *Cactus*, *Gladiolus*, and many more, is best extracted by weak alcohol. It is obtained as a dark red mass, yielding a bright red powder, soluble in water and weak alcohol. It is turned blue or green by alkalies, and is very fugitive. It is not known in a state of purity.

Another variety of red colouring matter is found in autumn in the leaves and fruit of certain plants. It has been called Erythrophyll, but its properties are little known.

3. BLUE COLOURING MATTERS.

These are found chiefly in flowers; also in some fruits and leaves. They are analogous to the red colouring matters of flowers, many, perhaps all, of which are naturally blue, but reddened by acids. They are turned green by alkalies; and many, such as the blue of *Viola odorata*, are used as tests of alkalinity. In some plants, such as *Crozophora tinctoria*, *Mercurialis annua*, *M. perennis*, &c. the juice, at first green, becomes blue on exposure to the air. In the first-mentioned plant, this change is hastened by exposure to ammoniacal vapours; and hence the resulting blue is probably azotized, as is the case with indigo. Unlike indigo, however, the blue of *Crozophora tinctoria* is reddened by acids.

The blue of the over-ripe fruit of *Rhamnus catharticus* is distinguished from the preceding by the action of alum, which, as well as alkalies, changes it to green.

4. GREEN COLOURING MATTER.

Chlorophyll.—This is the most abundant of all vegetable colouring matters, being found in the leaves, stalks, unripe fruit, and juice of all except the very lowest classes of plants, such as algæ, mosses, and sponges. It has been studied most recently by Berzelius.

It is extracted by ether, and purified by the successive action of alcohol and hydrochloric acid, from which last solvent it is precipitated by water. It forms a dark green mass, the powder of which is grass-green. Alcohol is its best solvent, but dissolves it sparingly. It is soluble in acids and alkalies, both of which it colours green. It is decolorised by chlorine. Berzelius has described two modifications of it, besides that above mentioned. It possesses few marked properties, although it has a tendency to combine with alkalies, such as lime, baryta, and oxide of lead. Its composition is unknown, as it has probably not been obtained in a state of purity. It may be considered as intermediate between fat or wax and the resins.

Polychrome.—This substance, in some respects analogous to the colouring matters, is found in several plants, as, for example, in the bark of the horse-chesnut and in quassia wood. It is dissolved by water, precipitated by acetate of lead, the precipitate decomposed by sulphuretted hydrogen, and the filtered liquid evaporated to the consistence of syrup. After some time the polychrome crystallises. It is purified by repeated solution in a mixture of alcohol and ether. It is sparingly soluble in cold, readily in hot water. The latter solution gelatinizes on cooling. A solution of polychrome appears colourless by transmitted light, but blue by reflected light; and exhibits a curious play of colours, visible when 1 part of polychrome is dissolved in 1,500,000 of water. Acids destroy this play of colours, alkalies increase it. According to Trommsdorff junior, its formula is $C_{16}H_9O_{10}$, or $C_{16}H_8O_9,HO$.

NON-AZOTISED VEGETABLE PRINCIPLES, THE TRUE NATURE OF WHICH IS NOT EXACTLY ASCERTAINED.

In the earlier works on vegetable chemistry, a number of substances were described under the general names of Extractive principle and Bitter principle. Later researches have shown that what was called Extractive principle is the result of the decomposition, probably of several substances, during the operations to which the vegetable was subjected; and that very many plants contain peculiar, often crystallisable compounds, having a bitter taste, and which are often doubtless the active principles of the vegetable in which they occur.

Few of these have been sufficiently examined; and the whole subject of these bitter non-azotised compounds, and of the changes they undergo, requires a thorough investigation, which would certainly throw much light on organic chemistry. The researches on Salicine and Phloridzine, compounds formerly described, and belonging to this class, have led to most important results, and have enabled us to classify these compounds; but our knowledge of the compounds now to be mentioned is too limited to enable us to adopt any system of classification, and we are compelled to confine ourselves to a brief descriptive catalogue of the more important among them.

Gentianine.—Extracted by ether from the root of *Gentiana lutea*, and purified by solution in alcohol. It forms golden yellow crystals, of a very bitter taste, which may be sublimed. According to Trommsdorff, when quite pure it is no longer bitter, and has acid properties, expelling carbonic acid from the alkaline carbonates, and forming with the alkalies golden-yellow crystallisable salts.

Absinthiine: from the flowers of wormwood, *Artemisia absinthium.* It is white and partly crystalline, intensely bitter, very soluble in alcohol. It may be combined with metallic oxides by double decomposition.

Santonine is found in the flowers of several species of *Artemisia*, and in the so-called *Semen Cynæ*, which is much used as a vermifuge, and is a mixture of the flowers, buds, and unripe seeds of these plants.

Four parts of this mixture are digested with one-half of slaked lime and 20 of alcohol at 90 per cent. The santonine is dissolved, in combination with lime and with a brown resin. It is separated by acetic acid, but is still contaminated with resin. This is removed by washing with a little alcohol; and the residue being dissolved in 8 or 10 parts of alcohol at 80 p. c. and boiled with animal charcoal, the liquid, on cooling, deposits santonine in colourless crystals, which must be kept in the dark, as they become yellow when exposed to light. It is tasteless and inodorous, fusible and volatilisable, sparingly soluble in water, more easily in alcohol and ether. It has acid properties, and forms salts with potash and soda, the latter of which crystallises. Acids dissolve it without altering it, and water precipitates from the solution the santonine unchanged. It forms crystalline salts with lime and baryta, and insoluble compounds with many metallic oxides. Its composition is represented by the formula C_5H_3O (Ettling); but its atomic weight must be twelve times greater, to judge from its capacity of saturation.

Populine is found in the bark and leaves of *Populus tremula*, along with salicine. It forms delicate white needles, which have a sweet taste like that of liquorice. It is sparingly soluble in water, readily in alcohol; and is reddened by oil of vitriol. (Braconnot; De Koninck.)

Liriodendrine is found in the bark of the root of *Liriodendron tulipifera.* (Emmet.) It forms white crystals, like those of boracic acid; sparingly soluble in water, more soluble in alcohol, with a bitter and balsamic taste.

Picrolichenine.—Discovered by Alms in the lichen *Variolaria amara*, from which it is extracted by alcohol. It is purified from a green matter which accompanies it by washing with a dilute solution of carbonate of potash. It forms obtuse double four-sided pyramids, which have a most intense bitter taste. When acted on by ammonia in a close vessel, it dissolves; and after some time the solution becomes yellow and deposits yellow crystals, which are not bitter. When the ammoniacal solution is exposed to the air, a dark red substance is formed, which indicates an analogy between this substance and orcine, which, as will be hereafter mentioned, occurs in other lichens. Its composition is unknown, but it contains no nitrogen. It is said to be powerfully febrifuge.

Cetrarine is analogous to the preceding. It occurs in several lichens, as in Iceland moss, *Cetraria Islandica*, and in *Sticta pulmonacea.* It is extracted by alcohol. It forms a fine white powder, very bitter to the taste. Concentrated hydrochloric acid colours it deep blue. Its other properties are little known, but it is said to be used as a febrifuge in Italy.

Elaterine is the active principle of Elaterium, the inspissated juice of the fruit of *Momordica elaterium.* The elaterium is dissolved in hot alcohol, and the concentrated solution thrown into water, which precipitates the elaterine. By repeating this process it is obtained pure. (Morries.) It forms delicate silky crystals of a very bitter taste. One sixteenth of a grain acts as a drastic purgative. Its composition is unknown. It merits a more minute examination.

Colocynthine.—The bitter and purgative principle of colocynth, which is the pulp surrounding the seeds of *Cucumis colocynthis.* It is obtained by evaporating the infusion made with cold water, at first in oily drops, which afterwards solidify into a brown brittle mass. It is soluble in water, alcohol, and ether, intensely bitter, and acts as a drastic purgative. Its chemical characters are imperfectly known, and it is probably a mixture.

Bryonine.—Obtained by a somewhat similar process from the juice of the root of *Bryonia alba* and *B. dioica.* It forms a brown or yellowish white mass, having a taste at first sweetish, then acrid and very bitter; soluble in water and alcohol, insoluble in ether. It appears to contain nitrogen, and is probably a mixture of several compounds. It is a drastic purgative and has poisonous properties.

Mudarine is found in the bark of the root of *Calotropis Mudarii.* (Duncan.) It is soluble in water and alcohol. The aqueous solution gelatinises when heated to 95°; at a higher temperature it is coagulated, the mudarine separating as a viscid mass. On cooling, it is slowly but completely redissolved. Mudarine has powerful emetic properties.

Scillitine.—Obtained from the juice of squills, the bulb of *Scilla maritima.* A brittle mass, of a nauseous bitter taste. It acts as an emetic and as a purgative, and appears to be poisonous. (Tilloy.)

Cathartine.—Similar to the preceding. Obtained from the leaves of *Cassia Senna* and *C. lanceolata*, and from some other plants. It has a bitter nauseous taste, and purgative properties.

Antiarine.—Formula $C_{14}H_{10}O_5$. (Mulder.) Is the active principle of the Upas poison, or Upas antiar, which is a gum-resin derived from *Antiaris toxicaria*, a tree found in Borneo, Sumatra, and Java. The Upas contains 3·56 per cent. of antiarine. It forms small scaly crystals soluble in 250 parts of cold water, 70 of alcohol, and 2790 of ether. It dissolves in 27·4 parts of hot water. It has neither acid nor alkaline properties. It is a frightful poison, and infallibly causes death, even when introduced into a wound in small quantity; the fatal event being preceded by vomiting, diarrhœa, and convulsions. No antidote is known.

Xanthopicrine is found in the bark of *Xanthoxylum Clava Herculis.* It forms greenish yellow silky crystals, intensely bitter and astringent. It is very soluble in alcohol, and has neither an acid nor an alkaline reaction. Its action on the system has not been studied, but the bark is used as a remedy in the Antilles.

Columbine.—Obtained from Columbo, the root of *Menispermum palmatum.* It is extracted by alcohol or ether. Forms colourless and transparent oblique rhombic prisms, or delicate white needles: is neutral, fusible, and contains no nitrogen. It is very bitter, and becomes still more so when dissolved in acetic acid. It is the active principle of columbo. (Wittstock.)

Quassiine is the bitter principle of the wood of *Quassia amara.* When pure, it forms small white opaque prisms, which are intensely bitter, and very soluble in alcohol. From the analysis of Wiggers, its formula is probably $C_{20}H_{12}O_6$.

Lupuline is the bitter principle of hops, the female flowers of *Humulus lupulus.* It is neutral, uncrystallisable, soluble in water and alcohol, and very bitter.

Lactucine is the active principle of *Lactucarium*, the inspissated juice of *Lactuca sativa*, *L. virosa*, and *L. scariola.* It forms yellowish indistinct crystals, which have a strong persistent, bitter taste. It is sparingly soluble in water, very soluble in alcohol. The anodyne effects of lactucarium are most probably to be ascribed to lactucine.

Ergotine.—Discovered by Wiggers in the Ergot of rye, *Secale cornutum.* It is obtained as a brown powder, of a pungent and bitter taste, and is conceived by Wiggers to be the active principle. He describes it as narcotic and poisonous; but its composition and properties are unknown, and it is most probably a mixture.

Porphyroxine.— Discovered by Merck in Bengal opium. It forms small brilliant crystals, which, when dissolved in diluted mineral acids and heated, yield a red colour. It is neutral, soluble in alcohol and ether, insoluble in water. It is quite distinct from the other crystalline substances found in opium, but as yet has been little examined.

Saponine is found in the root of *Saponaria officinalis* and *Gypsophila Struthium.* It is extracted by alcohol, and purified by repeated crystallisation from that solvent. It forms a white brittle mass, not crystallised. It has a taste at first sweetish, then acrid and irritating, and the smallest quantity of the powder introduced into the nostril causes violent sneezing. It is soluble in water; and the solution, even when very dilute, froths like a solution of soap. The root is used as a detergent.

Saponic Acid is produced by the action of acids and alkalies on saponine. It appears as a white powder, sparingly soluble in water, soluble in alcohol, and has very feeble acid properties. Its formula is $C_{26}H_{23}O_{12}$. (Frémy.)

Smilacine: Syn. *Parilline*, *Salseparine.* — Extracted by alcohol from *Sarsaparilla* (*Smilax sarsaparilla*). It is crystallisable, soluble in hot water and alcohol, colourless and tasteless. Its solutions have the property of frothing. Its formula appears to be

$C_{15}H_{13}O_5$. (Poggiale; Thubœuf; Petersen.) The Chinova bitter of Winkler, found in *China nova*, has been shown by Buchner jun. to be identical in its properties with smilacine; and Petersen has shown that its formula is $C_{15}H_{12}O_4$, differing from that of smilacine only by 1 eq. of water.

Senegine: Syn. *Polygaline*, *Polygalic Acid.* — Is found in *Polygala senega* and *P. virginea.* It is a white powder, at first tasteless, afterwards very acrid, and causing a feeling of astringency in the gullet. It also acts as a sternutatory. According to Quevenne, its formula is $C_{11}H_{18}O_{11}$.

Guaiacine.—Discovered by Trommsdorff in the wood and bark of *Guaiacum officinale.* It forms a yellow brittle mass, which has a sharp acrid taste. It is no doubt one of the active principles of the gum-resin of guaiacum, and is the cause of its acrid taste.

Plumbagine occurs in the root of *Plumbago Europæa.* It is extracted by ether, and forms fine orange-yellow crystals, which at first have a sweet taste, followed by a burning acrid sensation. It is neutral, and soluble in hot water. Alkalies give to its solution a cherry-red colour, but acids restore the yellow. The root also contains a peculiar fat, not yet investigated, which gives to the skin a lead-grey colour, whence the name of the plant is derived.

Cyclamine: Syn. *Arthanitine.* — Found in the root of *Cyclamen Europæum.* It crystallises in fine white needles, of a burning acrid taste, and having emetic and purgative properties.

Peucedanine.—Discovered by Schlatter in the root of *Peucedanum officinale.* Extracted by alcohol. It forms delicate white prisms, fusible, insoluble in water, soluble in alcohol and ether. The solution has an acrid burning taste. It is neutral. Formula, C_4H_2O. In some roots, that had been long kept, Erdmann found a modification of peucedanine, differing from it only in being insoluble in ether. Its formula was $C_8H_4O_3$; which only contains 1 at. of oxygen more than the formula of peucedanine doubled, and was, therefore, probably formed from it by the action of the atmosphere.

Imperatorine.—Found by Osann in the root of *Imperatoria Ostrutium.* Is extracted by ether. It forms long transparent prisms, has an acrid burning taste, is neutral, fusible, insoluble in water, soluble in alcohol and ether. Formula, $C_{24}H_{12}O_5$. (F. Dœbereiner.)

Phillyrine occurs in the bark of *Phillyrea media* and *latifolia*. It forms silvery scales, at first tasteless, afterwards bitter.

Fraxinine.—Found in the bark of *Fraxinus excelsior*. Fine six-sided prisms, soluble in water and alcohol. It has a bitter taste, and is neutral.

Tanghinine.—Extracted by ether from the seeds of *Tanghinia Madagascariensis* after the fixed oil has been removed by pressure. It is crystallisable; soluble in water, alcohol, and ether; very bitter and acrid. It is also poisonous. (Henry and Ollivier.)

Melampyrine.—Found by Hünefeldt in *Melampyrum nemorosum*. It forms white prismatic crystals, devoid of taste and smell, and perfectly neutral.

Meconine.—Discovered by Couerbe in opium. It is dissolved, along with most of the other ingredients of opium, when water is used as the solvent; and, being soluble in water, it remains dissolved when morphia, narcotine, &c. are precipitated by ammonia. Part of it, however, falls along with the precipitate. It is purified by the alternate action of alcohol, water, and ether; in all of which it is soluble with the aid of heat. When pure, it forms fine white prisms, which are at first tasteless, afterwards acrid. It is fusible, and may be sublimed unchanged. It requires for solution 266 parts of cold water, and 18 parts of boiling water. When heated with water, it first melts into an oily fluid, and gradually dissolves. Sulphuric acid, diluted with half its weight of water, dissolves meconine, forming a colourless solution, which when heated becomes dark green. Water throws down from the green solution brown flocks, which dissolve in alcohol with a rose-red colour. From this alcoholic solution the salts of alumina, lead, and tin throw down fine red lakes. Meconine is quite neutral. Its formula, according to Couerbe, is $C_{10}H_5O_4$, or rather the half of this; but its composition cannot be considered as ascertained. By the action of chlorine it is converted into mechloic acid, and nitric acid changes it into nitro-meconic acid.

Mechloic Acid is formed, along with a resinous matter, when chlorine gas is made to act on fused meconine. When pure, it forms colourless crystals, strongly acid, which contain no chlorine. Its formula, according to Couerbe, is $C_{14}H_7O_{10}$.

Nitro-meconic Acid is formed by the action of strong nitric acid, aided by a gentle heat, on meconine. It crystallises from its solution in hot water in regular yellow crystals. These are soluble in strong acids without change; but the addition of water destroys the yellow colour, and the acid is then deposited in colourless crystals. Alkalies dissolve it with a strong reddish yellow colour. According to Couerbe, its formula is $C_{20}H_9NO_{12} = C_{20}H_9O_7 + NO_5$ or $C_{20}H_9O_9 + NO_3$.

Cubebine.—Found by Soubeiran and Capitaine in Cubebs pepper (the seeds of *Piper Cubeba*). It is neutral, crystallisable, tasteless, sparingly soluble in water and alcohol. Its formula is probably $C_{34}H_{17}O_{10}$.

Olivile.—Found by Pelletier in the gum-resin of *Olea Europæa.* It forms white needles, which have an acrid, sweet, and bitter taste. It is fusible, soluble in hot water and alcohol, insoluble in ether. It is neutral. Formula, $C_{12}H_9O_4$. (Pelletier.)

Olivine is the name given by Landerer to a bitter substance obtained by him in the form of white crystals from the leaves of *Olea Europæa.* It is soluble in acids, but does not form crystallisable salts with them.

Amanitine is the poisonous principle of certain mushrooms, such as *Agaricus muscarius*, *A. bulbosus*, and others. It is not known in a pure state, and has only been obtained as a brown mass, the chemical properties of which are very imperfectly known.

The following substances are neutral, have generally a bitter taste or are tasteless, and are to a certain extent problematical, as the observations regarding them are very imperfect. It is probable that many of them will be found identical with some of the preceding.

Alcornine, from Alcornoco, the root of *Hedwigia virgelioides.*
Alismine, from *Alisma Plantago.*
Arnicine, from *Arnica montana.*
Asclepine, from the root of *Asclepias gigantea.*
Buenine, from the bark of *Buena hexandra.*
Canelline, from the bark of *Canella alba.*
Cascarilline, from the bark of *Croton Eleutheria.*
Cassiine, from *Cassia fistula.*
Centaurine, from *Erythræa Centaurium.*
Colletine, from *Colletia spinosa.*
Coriarine, from *Coriaria myrtifolia.*
Cornine, from the bark of the root of *Cornus florida.*
Corticine, from the bark of *Populus tremula.*
Cytisine, from the seeds of *Cytisus Laburnum.*

Daphnine, from the bark of *Daphne Mezereum* and other species. It is crystallisable.
Datiscine, from *Datisca cannabina.*
Diosmine, from the leaves of *Diosma crenata.*
Euonymine, from the seeds of *Euonymus Europæus.*
Fagine, from *Fagus sylvatica.*
Geraniine, from the *Geraniaceæ.*
Granatine, from unripe Pomegranates.
Guacine, from Guaco leaves.
Hesperidine, from the spongy part of the orange rind. Crystallises.
Hyssopine, from *Hyssopus officinalis.*
Ilicine, from *Ilex aquifolium.* Crystallisable.
Lapathine, from *Rumex obtusifolius.*
Ligustrine, from the bark of *Ligustrum vulgare.*
Lilacine, from *Syringa* or Lilac.
Menyanthine, from *Menyanthes trifoliata.*
Narcitine, from *Narcissus pseudo-narcissus.*
Primuline, from the root of *Primula veris.*
Pyrethrine, from the root of *Anthemis Pyrethrum.*
Rhamnine, from *Rhamnus frangula.*
Scordine, from *Teucrium Scordium.*
Scutellarine, from *Scutellaria lateriflora.*
Serpentarine, from *Aristolochia serpentaria.*
Spartiine, from *Spartium monospermum.*
Spigeline, from the root and leaves of *Spigelia anthelmia.*
Tanacetine, from *Tanacetum vulgare.*
Taraxacine, from *Leontodon Taraxacum.*
Tremelline, from *Tremella mesentherica.*
Zedoarine, from the root of *Curcuma aromatica.*

LECANORINE.—ORCINE.—ERYTHRINE.

We shall here describe, in a separate section, a remarkable class of vegetable products, which are colourless, and contain no nitrogen, but on exposure to the air in contact with ammonia yield beautiful colouring matters, in which nitrogen is an essential element.

To this class of colouring matters belong those of Archil and Litmus; and the study of them forms a very proper introduction to that of Indigo, and, through Indigo, to the study of the azotised principles of the vegetable kingdom.

Under the names of Orcine and Erythrine, Robiquet and Heeren have described certain colourless compounds obtained from several lichens, such as *Variolaria orcina*, *Lichen roccella*, and *Lecanora tartarea*. But all these substances demand a new investigation, as will appear from the following details, derived from the recent experiments of Schunck.

According to Schunck, when certain lichens, especially *Variolaria lactea*, are acted on by ether, which is best done by the method of displacement, a crystalline substance is obtained, to which he has given the name of *Lecanorine*. It is purified from a greenish matter by washing with cold ether, and crystallisation from its solution in alcohol. It is then white, insoluble in water, easily soluble in hot alcohol, also in ether and acetic acid.

In contact with alkalies at the ordinary temperature, it slowly undergoes a remarkable change, which takes place instantaneously at 212°. It is resolved into carbonic acid, and a new compound, which is identical with the orcine of Robiquet. This decomposition is best shown by dissolving lecanorine to saturation in cold barytic water, and heating the solution to the boiling point. There is instantly formed a copious precipitate of carbonate of baryta; and the liquid contains nothing but pure orcine, which crystallises on evaporation.

When lecanorine is boiled for a long time with water, it undergoes the same change, being gradually dissolved. The liquid is found to contain pure orcine.

A solution of lecanorine, mixed with ammonia and exposed to the air, gradually acquires a most intense and beautiful blue colour. In this case it is probably first changed, as by other alkalies, into orcine.

Schunck obtained from the same lichens two other compounds. The first is obtained by boiling them with alcohol, distilling off the alcohol from the filtered liquid, and treating the residue with boiling water, which on cooling deposits crystals. These are identical with the pseudo-erythrine of Heeren. They are soluble in alcohol, insoluble in ether, and nearly insoluble in cold water. According to an analysis made by Schunck, the formula of this substance is $C_{10}H_6O_4$. In contact with ammonia, this compound yields very slowly a red colouring matter. It dissolves in barytic water; and the solution, when boiled, yields carbonate of baryta. The remaining liquid has not been studied.

The other compound is obtained by acting on the lichens, previously exhausted by ether, with hot alcohol, which deposits on cooling white crystals, mixed with a greenish matter, which is easily removed by ether. This compound is soluble in alkalies, and is precipitated unchanged by acids. It differs from the preceding in its properties and composition.

It is probable, considering the facility with which lecanorine is decomposed by the action of hot water, that the two compounds just described are, like orcine, products of the decomposition of one or two substances originally present, which are altered even by boiling alcohol. From a quantity of lichen, which had long lain in a damp place, Schunck obtained no lecanorine, but a crystallisable substance resembling closely the last described.

It is hence obvious, that, in order to study successfully these singular compounds, we must endeavour to obtain the original compounds, such as lecanorine appears to be; and that we cannot expect to understand them if we confine our investigations, as was done by Robiquet and Heeren, and more recently by Kane, to products of decomposition, as the above experiments have demonstrated orcine to be, and as is probably the case with the erythrine and pseudo-erythrine of Heeren and Kane, in the preparation of which hot water is employed.

Orcine.—This substance was discovered by Robiquet, who found it in the *Variolaria orcina,* and considered it as pre-existent in that lichen. It has been shown above to be a product of the decomposition of lecanorine.

Orcine forms large regular four-sided prisms, soluble in water and alcohol. The aqueous solution has a sweet taste. The crystals are fusible at 212°, and may be sublimed into a liquid, which, in contact with water, is reconverted into crystals of orcine.

Orceine.—Orcine dissolves in the fixed alkalies, and the solution becomes brown on exposure to the air. But, when dissolved in ammonia, it gradually acquires a deep blood-red colour, and there is formed a compound of ammonia with a new substance, *orceine,* which contains nitrogen as an essential element, besides that of the ammonia. On the addition of acetic acid, orceine is precipitated as a brownish red powder.

Orceine is soluble in ammonia with a blood-red colour, in fixed alkalies with a violet-red tint, and is precipitated unchanged by acids. With the salts of lead and silver the ammoniacal solution gives deep red precipitates.

Robiquet has shown, that, during the conversion of orcine into orceine, oxygen is absorbed, and orceine is the only product, except water.

It is obvious that the composition of orcine must be closely related to that of lecanorine, from the fact that the latter is decomposed into the former, with the formation of carbonic acid. The analyses of orcine by Dumas, Will, and Schunck admit of two formulæ for that substance in its crystallised state. These are, $C_{16}H_{11}O_7$ and $C_{18}H_{12}O_8$.

In like manner, the analyses of lecanorine by Schunck admit of two formulæ, of which one is $C_{18}H_8O_8$ and the other $C_{20}H_9O_9$.

The latter formula for lecanorine agrees with the second for orcine; for $C_{20}H_9O_9 + 3HO - C_2O_4 = C_{18}H_{12}O_8$. But, notwithstanding this agreement, Schunck has shown, by determining the amount of carbonic acid formed when lecanorine is converted into orcine, that the other formulæ are the true ones. He found that the carbon of the carbonic acid separated was to the whole carbon of the lecanorine exactly as 1 to 9. Consequently the lecanorine cannot contain more than 18 atoms of carbon, and the orcine cannot contain more than 16. According to this view, 1 atom lecanorine $= C_{18}H_8O_8$ is resolved into 2 atoms carbonic acid $= C_2O_4$ and 1 atom *anhydrous* orcine $= C_{16}H_8O_4$; to this are added 3 atoms water $= H_3O_3$ to produce 1 atom crystallised orcine $= C_{16}H_{11}O_7$.

This enables us easily to explain the formation of orceine, the formula of which, according to the analysis of Dumas, is $C_{16}H_9NO_7$; for 1 atom crystallised orcine, $= C_{16}H_{11}O_7$, with the addition of 1 eq. ammonia NH_3, and 5 eq. oxygen $= C_{16}H_{14}NO_{12}$; and if from this sum 5 atoms water $= H_5O_5$ be removed, there remains 1 atom orceine $= C_{16}H_9NO_7$.

According to Robiquet, the Variolaria dealbata, when boiled with alcohol, yields a decoction in which orcine is contained; but it deposits on cooling crystals of another substance, which has not been further examined.

When the alcoholic solution of this lichen is evaporated to dryness, and the orcine removed from the extract by hot water, ether extracts from the residue another crystalline substance, which Robiquet calls Variolarine. It is fusible, and may be sublimed without much change.

Both these substances resemble those described by Schunck;

but our knowledge of all of them is too limited to allow us to pronounce them identical, although their identity is highly probable.

Erythrine and *Pseudo-erythrine.*—Heeren gave these names to two substances which he obtained from *Parmelia roccella* and *Lecanora tartarea.* They both possess the property of forming red colouring matters in contact with air and ammonia. Kane has recently investigated the same subject, but has unfortunately caused a confusion by altering the names; as he calls Heeren's pseudo-erythrine ‘Erythrine,’ and his erythrine ‘Erythriline.’

The Erythrine of Kane (Pseudo-erythrine of Heeren) is obtained by boiling the lichens with alcohol, evaporating to an extract, and boiling with water, which on cooling deposits it in large white scales. When the boiling is long continued, fewer crystals are obtained; so that it appears as if this substance, like lecanorine, were destroyed by boiling with water. Kane has not ascertained what products are formed when the crystals disappear.

To obtain Kane's Erythriline, (Erythrine of Heeren,) the alcoholic extract, after extraction by boiling water, is dissolved in weak potash, and the solution precipitated by hydrochloric acid. The precipitate is dissolved in weak ammonia, mixed with chloride of calcium to separate roccellic acid, and the filtered solution again precipitated by hydrochloric acid. The precipitate is Erythriline. It forms a yellowish or greenish, hardly crystalline powder. When boiled with water, it yields a brown bitter solution, containing a new substance, the bitter of Erythrine (Heeren), Amarythrine (Kane).

The Erythrine of Heeren, however, appears not to be identical with Kane's Erythriline; the former being soluble, the latter insoluble, in ether.

According to Heeren, his Erythrine passes into the bitter compound before yielding the red colour; but his Pseudo-erythrine forms the red compound without passing through this intermediate stage. But Kane states that the latter, which he calls Erythrine, readily yields the bitter compound. Heeren states that the bitter is formed without the access of air; while, according to Kane, the absorption of oxygen is essential to its production.

The bitter compound, Amarythrine of Kane, when its aqueous solution is exposed to the air, gradually passes into a crystalline compound, called by Kane *Telerythrine.* From his analyses of these compounds Kane deduces the following formulæ:

Erythriline . . .	$C_{22}H_{16}O_6$
Erythrine . . .	$C_{22}H_{13}O_9$
Amarythrine . .	$C_{22}H_{13}O_{14}$
Telerythrine . .	$C_{22}H_{10}O_{19}$

It is obvious that a renewed investigation is required before the conflicting statements of Kane and Heeren can be reconciled, or before the true nature and relations of all these substances can be understood; and it is much to be regretted that Kane should have added to the difficulty by the changes he has made in the names of the substances, which he supposes to be the same as those described by Heeren.

ARCHIL.—CUDBEAR.—LITMUS.

These are the names given to the dye-stuffs prepared in different countries, from the lichens above mentioned, by exposing them to the air in contact with putrefying urine or ammoniacal solutions. By this means the colour is developed, and a great part separates as a powder, while some remains dissolved. It is either dried for use, or thickened by the addition of chalk or gypsum.

The best Archil is prepared as above from the *Roccella tinctoria*, which is found in the Canary Islands, the Azores, Corsica, and Sardinia. When a mixture of carbonate of potash and ammonia is employed in the preparation, and chalk, &c. is afterwards added, the colour is rendered more blue by the alkali, and is named Litmus. Cudbear is chiefly prepared in England from *Lecanora tartarea* and *Parmelia omphalodes*. It is called Persio in Germany.

According to Kane, who has lately examined these substances, archil contains two colouring matters, Alpha-orceine and Beta-orceine, which differ only in the proportion of oxygen. The former is $C_{18}H_{10}NO_5$; the latter $C_{18}H_{10}NO_8$. Kane considers beta-orceine to be the same as orceine; but it will be seen that there is a difference between the formulæ of these compounds, as given by Kane and Dumas. Nevertheless, it must be observed that the formulæ of Kane's two varieties of orceine are easily deduced from that of anhydrous *orcine*, according to Dumas, by the addition of ammonia and oxygen. Anhydrous orcine, according to Dumas, is $C_{18}H_7O_3$. Now, if to this we add $NH_3 + O_5$, we shall have the formula of beta-orceine.

The properties of alpha-orceine and beta-orceine are the same as those of orceine. They have all a deep red colour, are sparingly soluble in water, and are separated from the solution by the addition of a neutral salt. In alkalies they dissolve with a magnificent purple colour.

Besides orceine, archil contains a red substance of an oily aspect, which Kane calls Erythroleic acid; and another compound, called Azoerythrine; besides a yellow matter, noticed by Heeren.

Litmus contains, according to Kane, four distinct compounds; namely, Erythroleine, Erythrolitmine, Azolitmine, and Spaniolitmine.

Erythroleine is liquid at 212°; soluble in alcohol, ether, and alkalies, with a purple colour. Formula, $C_{26}H_{22}O_4$.

Erythrolitmine is red; sparingly soluble, like the preceding, in water; soluble in hot alcohol. It dissolves in alkalies with a blue colour. Formula, $C_{26}H_{23}O_{18}$.

Azolitmine is insoluble in water and alcohol, soluble in alkalies. It is the chief ingredient of litmus, and corresponds to beta-orceine, from which it differs in containing 2 at. of oxygen more. Formula, $C_{18}H_{10}NO_{10}$.

Spaniolitmine contains no nitrogen. It is rarely present, has a bright red colour, and is soluble in alcohol and ether. Formula, $C_{18}H_7O_{16}$.

According to Kane, the ingredients of archil and litmus are in a continual state of transition, probably from the action of oxygen.

Alpha-orceine and *Beta-orceine*, when dissolved in ammonia, are decolorised by contact with metallic zinc, and an excess of ammonia precipitates white compounds which become purple in the air. They contain oxide of zinc, combined, according to Kane, with alpha-orceine and beta-orceine. It is probable, however, that the body in combination with the zinc contains less oxygen, as it acquires colour when exposed to the air.

According to Gélis, when litmus is dissolved in weak potash, and the blue solution precipitated by acetate of lead, the precipitate decomposed by sulphuretted hydrogen gives a mixture of sulphuret of lead with three colouring matters. Ammonia separates them from the sulphuret, and the addition of acetic acid precipitates the colouring matters in the form of a fine red powder. Ether extracts from this a reddish orange crystalline substance. From the residue alcohol dissolves a blood-red compound, and leaves a mass insoluble in water, which, when burned, leaves ashes. It dissolves in alkalies with a blue colour. All three contain nitrogen.

The natural colour of the ingredients of archil and litmus seems to be red, but it is turned blue or purple by the presence of alkalies.

These dye-stuffs yield very brilliant but fugitive colours to cloth. They are chiefly used to heighten the bloom of other dyes.

The reader will observe the analogy between the substances now described, and the coloured compounds formed by the action of air and ammonia on salicine and phloridzine as formerly described.

INDIGO.

We shall describe this remarkable substance in the pure state, with the numerous products arising from it, in the first instance; after which the formation of the indigo of commerce will be more easily understood.

To obtain pure Indigo, the commercial substance, in fine powder, is placed for several days in contact with green vitriol, hydrate of lime, and water, in a stoppered vessel. The best proportions are 5 parts of indigo, 10 of green vitriol, 15 of hydrate of lime, and 60 of water. The colour is destroyed, and the clear yellowish fluid is drawn off with a syphon, mixed with hydrochloric acid, and the blue precipitate which falls is well washed, first with pure water, and then with boiling alcohol, until the latter solvent no longer acquires any colour, or only a pure blue; it is then dried in the air. Instead of the above mixture a solution of 1 part of caustic soda and 1 of grape-sugar in 20 of water may be employed to dissolve the indigo.

Pure indigo forms a deep blue powder, which acquires a coppery lustre when rubbed with a smooth body. It is quite insoluble in water, alcohol, ether, fixed and volatile oils, hydrochloric acid, and diluted alkalies. It dissolves in oil of vitriol with a deep blue colour; and with anhydrous sulphuric acid it forms a reddish purple mass, which dissolves in water without developing heat, and forms a deep blue solution. By the action of nitric, chloric, and chromic acids, of chlorine and bromine, it is changed, becomes yellow, and yields a multitude of new products, which dissolve with a yellow colour in water and alcohol. It is also decomposed when heated with a strong solution of caustic potash. It is decolorised and dissolved by contact with many deoxidising agents, such as protoxides of iron, tin, and manganese, if a soluble alkaline base be present; and undergoes the same change in contact with alkalies and grape-sugar. In the latter case, formic acid is produced. When thus dissolved, white indigo is formed.

When thrown in small quantity on a heated plate of platinum, indigo is totally sublimed, without charring, in the form of purple vapours which condense into purple crystals. When a large quantity is heated, the lower part is charred, and the crystals which are formed condense on the upper surface, from which they are easily separated.

White Indigo. — To obtain this compound, the yellow alkaline solution above described as prepared from common indigo is carefully protected from the access of air, both before and after the addition of the hydrochloric acid. The precipitate is well washed with recently boiled water, or with diluted sulphurous acid, rapidly drained on a filter, and dried on the filter in the vacuum of an air-pump. When the process is well performed, there is obtained a grey mass, sometimes slightly blue on the surface, which is formed of minute crystals.

White indigo is insoluble in water and diluted acids; soluble in alkalies, alcohol, and ether, to which it gives a yellow colour. When exposed to the air, it becomes blue from the absorption of oxygen; rapidly if moist, more slowly in the dry state: and its solutions, when exposed to the air, deposit blue indigo as a fine powder.

The solutions of white indigo in alkalies precipitate many metallic salts. These precipitates, when they are not blue at first, become so on exposure to the air. According to Runge, the precipitate formed by white indigo in solutions of sesquioxide of iron yields, when heated, a green crystalline sublimate; that formed with salts of black oxide of copper, a yellow sublimate, also crystalline; that formed in solutions of silver, orange-yellow crystals; and that formed in solutions of binoxide of mercury, grass-green crystals. These sublimates require a more minute investigation, especially as the results of Runge differ from those of other experimenters.

COMPOSITION OF BLUE AND OF WHITE INDIGO.

The first accurate analysis of blue indigo was made by Crum, and has been confirmed by Dumas and by Erdmann. Its formula is $C_{16}H_5NO_2$. White indigo, according to Dumas, is $C_{16}H_6NO_2$; so that they differ only by 1 eq. of hydrogen. Two views may be taken of their relation to one another. According to the first, white indigo is blue indigo *plus* 1 eq. hydrogen; just as hyduret of benzule is benzule + 1 eq. hydrogen. According to the other, white indigo is the hydrate of a compound containing 1 eq. less oxygen than blue indigo. Thus, blue indigo $= C_{16}H_5N + O_2$, and white indigo $= C_{16}H_5N + O + HO$. They would thus be viewed as oxides of a common radical, $C_{16}H_5N$, the protoxide being hydrated.

The fact, that white indigo is produced by the deoxidising agency of grape-sugar, speaks strongly in favour of the latter view; for, were white indigo a hyduret of blue indigo, it could only be formed here by the decomposition of water, the hydrogen of which would unite with the blue indigo to form white indigo, while its oxygen would again unite with the hydrogen of the sugar. It is highly improbable that oxygen should quit hydrogen to unite with the same element.

Moreover, white indigo combines with oxides; and, like other substances which do so, it probably combines with basic water when separated from a fixed base. On the whole, therefore, while both views deserve attention, we incline to the latter; and the reader will not fail to remark, that the relation between blue and white indigo is the same, in all probability, as that between alloxan and alloxantine.

Blue indigo contains the elements of cyanogen, and benzule or benzile; for benzule $= C_{14}H_5O_2$, + cyanogen $= C_2N$, $= C_{16}H_5NO_2$. It is worthy of remark, that when benzile is heated with caustic potash an indigo-blue colour is formed, which soon disappears.

ACTION OF SULPHURIC ACID ON INDIGO.

This subject has been investigated by Crum, Berzelius, and Dumas. It has been mentioned that indigo may be made to combine with anhydrous sulphuric acid, or with oil of vitriol. Fuming sulphuric acid also readily dissolves one-fifth of its weight of indigo, and, when mixed with water, no insoluble matter is separated. But when 1 part of indigo is dissolved in 8 parts of oil of vitriol, the addition of water separates a purple powder. The filtered solution contains, according to Berzelius, two acids, sulphoindigotic acid and hyposulphoindigotic acid; while the purple powder above mentioned is a third acid, the sulphopurpuric. All these acids yield, with alkalies, blue or purple salts, which are insoluble in saline solutions, but readily soluble in pure water. For this reason, when the acid solution of indigo is neutralized with acetate or carbonate of potash, the salts of potash separate as a bulky blue precipitate, which is called blue carmine or soluble indigo. The salts of hyposulphoindigotic acid are more soluble than those of sulphoindigotic acid.

When separated by means of sulphuretted hydrogen from their compounds with oxide of lead, these two acids are yellow and soluble in water, and their solutions absorb oxygen from the air, becoming blue.

When sulphoindigotate of potash is dissolved in 50 parts of lime water, and heated with contact of air, the solution becomes first purple, afterwards scarlet, and lastly pure yellow. According to Berzelius, these colours are owing to the successive production of four acids, which may be separated at the proper stages of the process. The first he calls purpurosulphuric, the second flavosulphuric, the third fulvosulphuric, and the fourth rufosulphuric acid. These compounds require a thorough investigation.

All the blue acid solutions just described, as well as their salts, are turned yellow by nitric acid, chlorine, and bromine.

The sulphopurpuric acid, (Phœnicine of Crum,) when well washed, dissolves in water with the same blue colour as the other two; but gives purple salts with bases, of which the salts of soda and ammonia are the most soluble.

According to Dumas, the action of sulphuric acid on indigo is analogous to its action on alcohol. The indigo loses 1 atom of water, and the residue combines with 2 atoms of sulphuric acid. The acid thus formed he calls sulphindylic acid, and compares it to sulphovinic acid, and the organic compound in it to oxide of ethule (ether). According to this view, blue indigo is the hydrate of an organic oxide, $C_{16}H_4NO + HO$; sulphindylic acid is $C_{16}H_4NO + 2SO_3 + HO$, and the salt of potash is $C_{16}H_4NO,SO_3 + KO,SO_3$. But as it is impossible in any way to reproduce indigo from these compounds, as alcohol may be reproduced from sulphovinic acid and its salts, this view is not very probable.

Moreover, if such be the composition of blue indigo, it is hardly possible to account for the production of white indigo, according to any known analogies.

The opinion is therefore much more probable, as well as more consonant to analogy, that the acids formed by the action of sulphuric acid on indigo contain, not sulphuric, but hyposulphuric acid, as is the case with isethionic and other acids.

According to Dumas, the sulphopurpuric acid is composed of 2 atoms indigo and 2 atoms sulphuric acid, which together neutralise 1 atom of base.

The whole subject of these acid compounds is still exceedingly obscure, and must continue so until further investigations shall have been made.

PRODUCTS OF THE OXIDATION OF INDIGO.

Isatine. — This remarkable compound is one of the products obtained when indigo is oxidised by means of sulphuric acid and bichromate of potash. It was discovered at the same time by Erdmann and by Laurent.

To obtain it, indigo, rubbed with water to a fine powder, is gently heated with a mixture of equal parts of sulphuric acid and of bichromate of potash, previously dissolved in 20 to 30 parts of water. The indigo dissolves, at first without effervescence, towards the end with a slight disengagement of carbonic acid, and yields a deep brownish yellow liquid, which on cooling deposits isatine in crystals. These are purified by recrystallisation, first from water, and finally from alcohol.

Isatine forms hyacinth-red or reddish-orange crystals, of a brilliant lustre, easily soluble in hot water and in alcohol. Its solutions stain the skin, and give it a disagreeable odour. It is decomposed by heat. Chlorine converts it into two new compounds, chlorisatine and bichlorisatine. When dissolved in alkalies, it is changed into isatic acid.

According to Erdmann and Laurent, its formula is $C_{16}H_5NO_4$; so that it represents blue indigo *plus* 2 atoms of oxygen.

Isatic acid.—Isatine dissolves in caustic potash with a purple colour, which passes into yellow on the application of heat. The liquid yields, on evaporation, isatate of potash as a crystalline salt, which, when recrystallised from alcohol, forms small, hard, colourless prisms. This salt gives with acetate of lead a white precipitate, isatate of lead; which, when decomposed by sulphuretted hydrogen, yields a solution of the acid. Isatic acid is deposited from this solution by spontaneous evaporation as a white powder, hardly crystalline.

It is soluble in cold water; but the solution when heated becomes yellow, owing to the production of isatine. The formula of the anhydrous acid in the salt of silver is $C_{16}H_6NO_5$, and it represents isatine *plus* 1 atom of water. It is therefore formed from isatine as benzilic acid is from benzile, but the atom of combined water is more easily separated.

According to Laurent, isatine forms with ammonia a salt, the acid of which contains 3 at. isatine + 2 at. water.

Isatyde.—When isatine is dissolved in hydrosulphuret of ammonium, there is deposited, on cooling, a yellowish white powder, not crystalline, which Erdmann calls Isatyde. It dissolves in ammonia and in the caustic alkalies with a dark red colour, which passes into yellow on the application of heat. The solution in potash deposits crystals, and gives with hydrochloric acid a flocculent yellow precipitate.

Erdmann gives, as the formula of isatyde, $C_{16}H_6NO_3$; according to which it is formed from isatine by the subtraction of 2 at. of oxygen and the addition of 1 at. of water. But, as Erdmann did not determine the amount of nitrogen, it is possible that a portion of ammonia may have entered into its composition. The formula $C_{16}H_5N_2O$ would agree equally well with the percentage of carbon and hydrogen obtained by Erdmann. On one occasion, when preparing isatyde with the mother liquid of a previous similar operation, Erdmann obtained a crystalline violet powder, the carbon and hydrogen of which agreed with the formula $C_{16}H_6N_2O$.

ACTION OF CHLORINE ON ISATINE.

When a solution of isatine is saturated with chlorine, two new compounds are obtained, which only differ from isatine in having a part of the hydrogen replaced by chlorine. They are called Chlorisatine and Bichlorisatine. Both are hardly soluble in cold water, and are separated by alcohol, in which the latter is rather more soluble than the former.

Chlorisatine.—Formula $C_{16}H_4ClNO_4$. It crystallises from alcohol in transparent four-sided prisms of an orange colour and a bitter taste. It may be partly sublimed. It dissolves in 50 parts of hot water. Sulphuric acid dissolves it without decomposition;

nitric acid destroys it. It causes no precipitate of chloride of silver in solutions of that metal.

Chlorisatic acid. — Chlorisatine is acted on by caustic potash exactly as isatine is. It dissolves at first with a deep red colour, which passes into yellow; and the solution deposits a bright yellow salt, the chlorisatate of potash. The acid, when separated from its salts, is instantly resolved into chlorisatine and water. Its formula, $C_{16}H_5ClNO_5$, explains this, as it is equivalent to chlorisatine + 1 atom of water. The salt of potash gives, with the solutions of silver and baryta, yellow crystalline salts; with solutions of lead, a brilliant yellow gelatinous precipitate, which shortly changes into a scarlet crystalline powder. The latter dissolves in hot water, and is deposited again in red crystals.

Bichlorisatine.—Formula, $C_{16}H_3Cl_2NO_4$. It forms small hyacinth-red crystals, rather more soluble in water and alcohol than chlorisatine, which it resembles very much in its characters.

Bichlorisatic acid.—It is formed exactly as chlorisatic and isatic acids are, by the action of caustic potash on bichlorisatine. The bichlorisatate of potash is yellow; as are the salts of baryta, silver, and lead, the latter permanently so. The salt of copper is, when first formed, of the colour of hydrated peroxide of iron; it then becomes pale greenish yellow, and finally carmine-red.

Bichlorisatic acid is more permanent than chlorisatic acid, and may be obtained from the salt of potash as a yellow powder. But when its solution is heated, or evaporated to dryness, the acid is resolved into its component parts, bichlorisatine and water. Formula $C_{16}H_4Cl_2NO_5$, = bichlorisatine, $C_{16}H_3Cl_2NO_4$, + 1 at. water, HO.

By the action of bromine on isatine there are formed two new compounds, *bromisatine* and *bibromisatine*, analogous in composition and properties to the preceding. Bibromisatine, treated with potash, yields *bibromisatic acid.*

It is to be observed that the action of chlorine on isatine is very analogous to its action on saliculous acid, and it is probable that the action of ammonia on the compounds thus produced will yield results similar to those obtained from the action of ammonia on the chloride of salicule.

Chlorisatyde.—When chlorisatine is dissolved with the aid of heat in hydrosulphuret of ammonium, the solution deposits, on cooling, a white or yellowish powder, hardly crystalline. This is called, by Erdmann, Chlorisatyde. It is sparingly soluble in water, and by heat is resolved into chlorisatine, water, and a new compound, *Chlorindine*, which appears as a violet powder. The formula of chlorisatyde is $C_{16}H_5ClNO_4$; that of chlorindine is $C_{16}H_5ClNO_2$.

Chlorisatyde dissolves in potash with a red colour, which passes into yellow; and the liquid now yields, on evaporation, a salt composed of potash and a new acid, *Chlorisatydic acid.*

Bichlorisatine, treated with hydrosulphuret of ammonium, yields analogous results, producing *bichlorisatyde;* and, from the action of potash on this, *bichlorisatydic acid.*

By the action of alcohol, saturated with sulphuretted hydrogen, on isatine and chlorisatine, Erdmann obtained two new compounds, which he calls *Sulphisatyde* and *Sulpho-chlorisatyde.* Their composition is not ascertained.

Chloranile.—By the action of chlorine on a warm alcoholic solution of chlorisatine or bichlorisatine, Erdmann obtained a new compound of carbon, oxygen, and chlorine, which he calls Chloranile. Its formula is $C_6O_2Cl_2$. It forms pale yellow pearly scales, soluble in hot alcohol, unaltered by acids, fusible and volatilisable without decomposition. When dissolved in caustic potash, half of its chlorine is replaced by oxygen, and *chloranilic acid* is formed, the formula of which is C_6O_3Cl. Chloranile dissolves in sulphuret of potassium, forming a yellow solution; which, when exposed to the air, passes through all shades of red, till at last it becomes purple and opaque from the separation of a black powder.

Chloranilic acid.—A hot solution of chloranile in potash deposits, on cooling, brownish purple brilliant prisms of chloranilate of potash. A solution of this salt, mixed with hydrochloric acid, gives reddish white shining scales of hydrated chloranilic acid, the formula of which is $C_6O_3Cl,HO + aq$. The solutions of the salts of this acid are commonly purple.

Chloranilammon and *Chloranilam.*—Chloranile dissolves in ammonia with a blood-red colour, and the solution yields crystals of *chloranilammon.* They are small chesnut-brown needles, which dissolve in hot water, tinging it purple. When this solution is mixed with hydrochloric acid, it does not yield chloranilic acid, but black needles of *chloranilam.*

The former compound contains the elements of 2 at. chloranilic acid and 2 at. ammonia, and in the crystals 9 at. of water of crystallisation. The latter contains the elements of 2 at. of chloranilic acid, 1 at. of ammonia, and 5 of water of crystallisation. They cannot be considered as salts of ammonia, for they do not contain, in the anhydrous state, the elements of water necessary to form oxide of ammonium; neither do they contain chloranilic acid, for their reactions with metallic salts are quite different from those of a chloranilate. By the action of alkalies they are changed into chloranilates, while ammonia is disengaged; and, when heated with mineral acids, they likewise yield ammoniacal salts, while chloranilic acid is separated.

When the product of the action of chlorine on a solution of chlorisatine or bichlorisatine, after the chloranile has been separated, is subjected to distillation, there remains a brown resinous mass, which, on being further heated, yields a semifluid oily product, often accompanied with a white crystalline sublimate. If the whole product be now redistilled with aqua potassæ, a solid substance is volatilised, and the residue dissolves. The solution deposits prismatic crystals, which are purified by repeated crystallisations from aqua potassæ. The solution of this salt, mixed with hydrochloric acid, yields a white flocculent precipitate, which volatilises with the vapours of boiling water and sublimes in needles. This compound is similar to one obtained by Erdmann among the products of the action of chlorine on indigo. He calls it *chlorinised chlorindoptenic acid;* and, from the analysis of the salt which it forms with oxide of silver, he deduces the remarkable formula, $C_{12}Cl_5$, for the anhydrous acid.

PRODUCTS OF THE ACTION OF CHLORINE ON INDIGO.

According to Erdmann, when powdered indigo, mixed with water, is exposed to the action of chlorine at a low temperature, it is completely decomposed, and yields an orange or brownish mass. When the whole is distilled, a white crystalline sublimate is obtained, which is a mixture of two new compounds, *chlorindatmit* and *chlorindoptenic acid.* The residue, boiled with water, yields a large quantity of chlorisatine and bichlorisatine, and there remains a resinous mass. The liquid, out of which the chlorisatine and bichlorisatine have crystallised, is acid from free hydrochloric acid, and contains sal-ammoniac.

Chlorindatmit.—When the mixed sublimate above described is distilled with carbonate of potash, chlorindatmit is obtained as a white sublimate, fusible and volatile, having an odour of fennel. Formula, $C_{12}H_4Cl_3O_2$.

Chlorindoptenic acid.—This acid remains combined with the potash, forming a crystallisable salt, which, when acted on by acids, yields chlorindoptenic acid in white flocks, of a nauseous smell. Its formula is $C_{12}H_2Cl_3 + HO$. It forms with oxide of silver a lemon-yellow insoluble salt, $C_{12}H_2Cl_3 + AgO$.

Erdmann gave to the mixed sublimate, containing the two preceding compounds, the name of *Chlorindoptene*. It appears to be a compound of the two in atomic proportion. Its empirical formula is probably $C_{24}H_7Cl_6O_3$. Erdmann deduced from his analysis, as the simplest expression of the results, the formula $C_8H_2Cl_2O$.

It is obvious that the action of chlorine on indigo is analogous to that of chromic acid already described, with the exception that the isatine, as might be expected, is converted into chlorisatine and bichlorisatine. It is not known whether the chlorindatmit and chlorindoptenic acid are formed directly from indigo, or by the action of hydrochloric acid on chlorisatine and bichlorisatine.

It may be interesting to give a tabular view of the singular compounds above described, for our knowledge of which we are indebted chiefly to the admirable researches of Erdmann.

Isatine	$C_{16}H_5NO_4$ (Erdmann, Laurent.)
Isatic acid	$C_{16}H_6NO_5+HO$
Chlorisatine	$C_{16}H_4ClNO_4$ (Erdmann, Laurent.)
Chlorisatic acid	$C_{16}H_5ClNO_5+HO$
Bichlorisatine	$C_{16}H_3Cl_2NO_4$ (Erdmann, Laurent.)
Bichlorisatic acid	$C_{16}H_4Cl_2NO_5+HO$
Bromisatine	$C_{16}H_4BrNO_4$
Bromisatic acid	$C_{16}H_5BrNO_5+HO$
Bibromisatine	$C_{16}H_3Br_2NO_4$
Isatyde	$C_{16}H_6NO_3$
Chlorisatyde	$C_{16}H_5ClNO_4$
Bichlorisatyde	$C_{16}H_4Cl_2NO_4$
Bichlorisatydic acid	$C_{16}H_5Cl_2NO_5+HO$
Chlorindine	$C_{16}H_5ClNO_2$
Chlorindoptene	$C_8H_2Cl_2O$
Chlorindoptenic acid	$C_{12}H_2Cl_3+HO$
Chlorindatmit	$C_{12}H_4Cl_3O_2$
Chloranile	$C_6Cl_2O_2$
Chloranilic acid	C_6ClO_3+HO
Chloranilammon	$C_{12}Cl_2O_6+2NH_3$
Chloranilam	$C_{12}Cl_2O_6+NH_3$
Chlorinised Chlorindoptenic acid	$C_{12}Cl_5$

PRODUCTS OF THE ACTION OF NITRIC ACID ON INDIGO.

Anilic acid: Syn. *Indigotic acid.* — This acid is formed when indigo is gradually added to boiling nitric acid, previously diluted with 12 or 15 parts of water. It is contaminated at first with an acid, oily-looking compound, and is purified by adding acetate of lead to the hot solution as long as it yields a brown precipitate. The filtered liquid deposits anilate of lead; which, when acted on by sulphuric acid, yields pure anilic acid.

It forms fine needles, colourless or yellowish white, which are fusible and volatilisable. Nitric acid converts it into oxalic and carbazotic acids. It requires 1000 parts of cold water for solution, but is far more soluble in hot water. Its formula, according to Dumas, is $C_{14}H_4NO_9 + HO$. It forms soluble and crystallisable salts with ammonia, and with the oxides of lead and silver.

Picric acid: Syn. *Nitropicric acid; Carbazotic acid.*—This acid is formed by the action of strong nitric acid, either on indigo, or on the preceding acid. It is also produced by the action of strong nitric acid on salicine, coumarine, silk, and some other substances.

One part of indigo is cautiously added, in very small portions, for fear of explosion, to 10 or 12 parts of hot nitric acid, of sp. g. 1·43. The mixture is boiled, if necessary, with more nitric acid, till red fumes no longer appear; and, on cooling, impure picric acid is deposited. It is purified by solution in potash and precipitation by nitric acid, and finally by recrystallisation from water.

It forms bright yellow scaly crystals, sparingly soluble in cold, easily in hot water; soluble in alcohol and ether. It has a very intense bitter taste. It is fusible and volatilisable when gently heated; but, when rapidly heated, it deflagrates.

According to Dumas and Marchand, the formula of the crystallised acid is $C_{12}H_2N_3O_{13} + HO$.

The salts of picric acid explode when heated, frequently with evolution of light. They are all bitter when soluble, and the picrate of potash has been used with success as a cure for intermittent fever. They have all likewise a yellow colour; and their general formula is $C_{12}H_2N_3O_{13} + MO$.

When the soluble picrates are left in contact with water, hydrate of lime, and green vitriol, they are decomposed, yielding a blood-red solution, which contains lime united with a new acid, the salts of which with the alkalies are soluble, bitter, and yield blood-red solutions.

A solution of picric acid in alcohol is used as a test for potash. If there be not too much water present, the picrate of potash, being very sparingly soluble, is deposited as a yellow crystalline precipitate; whereas the picric acid forms a very soluble salt with soda, and thus serves to distinguish these two alkalies from each other.

PRODUCTS OF THE ACTION OF ALKALIES ON INDIGO.

When powdered indigo is added to boiling aqua potassæ, sp. g. 1·45, it is easily dissolved, forming a deep reddish brown solution; which, when further evaporated, forms, on cooling, a solid crystalline mass. This dissolves in water; and the solution, when exposed to the air, deposits blue indigo. If the greater part of the potash in the freshly-made solution be neutralised by adding an acid as long as a bluish green precipitate is formed, there remains a golden-yellow solution, which, when filtered and acidulated with acetic acid, yields a kermes-coloured precipitate. This is called by Fritzsche *Chrysanilic acid.* It is purified by solution in ether, which, when evaporated, leaves it as a yellow mass. When boiled with diluted mineral acids, the solution becomes purple, deposits bluish black crystals, the nature of which is not yet ascertained; while a new acid, Anthranilic acid, remains in solution. As chrysanilic acid has not yet been obtained in a state of purity, its true formula is unknown.

Anthranilic acid.—This acid is prepared by dissolving indigo in hot aqua potassæ, sp. g. 1·35, and adding to the mixture powdered peroxide of manganese, till the liquid, when diluted and exposed to the air, no longer forms blue indigo. The solution now contains anthranilate of potash with a large excess of free potash. It is neutralised by sulphuric acid, and the anthranilate separated from the sulphate of potash by alcohol, which dissolves the former. The salt is decomposed by acetic acid, and yields impure anthranilic acid in orange crystals. It is now combined with lime; and, the anthranilate of lime being purified by recrystallisation, its hot solution is decomposed by acetic acid, and, on cooling, deposits hydrated anthranilic acid in tabular crystals half an inch in length, which are nearly colourless.

Anthranilic acid is fusible, and sublimes when gently heated, yielding crystals very similar to benzoic acid. When mixed with powdered glass and strongly heated, it is decomposed, and yields carbonic acid and an oily substance, *Aniline*, which is an organic base and contains no oxygen. (See the section on the organic bases.) Anthranilic acid is sparingly soluble in cold water, soluble in alcohol and ether.

Its formula, according to Fritzsche, is $C_{14}H_6NO_3 + HO$. It forms with lime a salt which crystallises in large transparent rhombs; and with oxide of silver, a salt, $C_{14}H_6NO_3 + AgO$, which is soluble in hot water and crystallises on cooling.

Indigo, in being converted into anthranilic acid, loses 2 atoms of carbon, and takes up the elements of 1 atom of water. What becomes of the carbon is not known.

COMMERCIAL INDIGO.

Indigo is obtained from many plants; as from the different species of Indigofera, I. tinctoria, I. anil, I. argentea, &c.; from Wrightea (Nerium) tinctoria, Isatis tinctoria or Woad, Pergularia tinctoria, Gymnema tingens, Polygonum tinctorium, Tephrosia (Galega) tinctoria, Amorpha fruticosa, &c.

In the plants indigo exists in the form of white indigo, and may be extracted in that form by water, alcohol, and ether. It is probably combined with a base to which it owes its solubility.

In North America the dried leaves are extracted by warm water, and the infusion exposed to the air, when it deposits blue indigo. In India and South America the fresh or half-dried plants are covered with water and allowed to ferment, when ammonia and carbonic acid are disengaged in abundance, and all the indigo is brought into the soluble state. As soon as a blue or coppery film appears on the surface of the water, it is drawn off, and agitated in open vessels till the blue indigo is deposited as a sandy powder. The powder is dried, and sold in the form of brittle cakes, easily reduced to powder, which, when rubbed with the nail, assume a copper colour. The stronger this colour is, the greater is the proportion of pure indigo present in the specimen examined.

It is never quite pure; and contains the following substances, besides blue indigo, according to Berzelius: 1. *Gluten of indigo*, which is dissolved out by diluted acids. 2. *Indigo-brown*, dissolved by caustic potash with the aid of a gentle heat: it resembles humic and apocrenic acids. 3. *Indigo-red*, which is dissolved, after the removal of the two preceding substances, by boiling alcohol. When heated, this substance yields a white sublimate, *deoxidised indigo-red*, which is reconverted into indigo-red by the action of nitric acid.

When these have been removed, indigo-blue remains, which is still impure, containing mineral substances. It is purified, as before described, by converting it into white indigo, dissolved in an alkali, and pouring the solution into diluted hydrochloric acid, when pure indigo-blue is deposited.

When indigo is distilled, it yields, according to Unverdorben, among a variety of other products, a volatile substance, called by him *Crystalline*, which is a base.—(See *Aniline.*)

For dyeing, indigo is dissolved, as before described, either by means of hydrate of lime, green vitriol, and water, or by caustic soda, grape-sugar, and water. In both cases it is converted into white indigo, which dissolves in the alkali with a wine-yellow colour. The cloth to be dyed is steeped in this solution, and exposed to the air; and the process is repeated till the desired depth of colour is attained. Other substances may be used to effect the reduction and solution of the indigo, such as bran and pearlash, or orpiment, lime, and pearlash. The indigo vat, as it is called, is improved by the addition of woad (which itself contains a little indigo, and was used for dyeing blue in Europe before the introduction of the latter) and of madder. An indigo vat, once set in action, may be kept so for several months by the occasional addition either of indigo or of the alkalies and reducing agents, according as one or other is exhausted.

The solution of indigo in sulphuric acid is also used in dyeing, under the names of *Saxon-blue* and *Soluble indigo.* The finest colour is obtained from the sulpho-indigotate of potash, acidulated with sulphuric acid.

The only method that can be at all depended on for ascertaining the relative values of different specimens of commercial indigo, is to ascertain the weight of the residue left, after the gluten, indigo-brown, and indigo-red have been removed by the successive action of boiling water, diluted acid, strong aqua potassæ with a gentle heat, and boiling alcohol, the action of the latter being repeated till it begins to acquire a pure blue colour. The residue contains only a small portion of mineral impurities. All other methods, such as that of bleaching by chlorine, give most inaccurate results.

COCHINEAL-RED—CARMINE.—KERMES.

Cochineal is the well-known dye-stuff, which is, in fact, an insect, (coccus cacti,) found on the leaves of a species of cactus in South America. It occurs in small round masses, nearly black, and covered with a fine white powder, which is said to be a sign of good quality.

The colouring principle, *cochineal-red*, or *cochenilline*, forms crystalline grains of a reddish purple, soluble in water and alcohol, insoluble in ether. The aqueous solution is turned orange by acids, violet by alkalies, and yields a beautiful lake with alum, which is known by the name of Carmine. The colour of carmine is heightened by the addition of a solution of tin.

Cochenilline contains nitrogen, but its true formula is unknown.

The finest crimson and scarlet dyes are made from cochineal, according as the mordant is alumina or tin.

Kermes is a dye-stuff similar in its origin and properties to cochineal, but inferior in beauty of tint. It is derived from *coccus ilicis*.

The red colouring matter of stick-lac, which is also used as a dye, has similar properties. Lac is produced on certain plants by the puncture of an insect.

ALOES.

This well-known drug is the inspissated juice of various species of *aloe*, and contains an azotised compound, distinguished from all others by its relation to nitric acid.

Commercial aloes dissolves readily in hot water and alcohol. The active principle has only been obtained in the form of a yellow extract, which in the original mass appears to be mixed with a brown matter of a resinous aspect, which, however, is soluble in hot water. Further experiments are required to ascertain the true nature of the natural ingredients of aloes; and it is highly probable that the resinoid portion is a product of the action of oxygen on the part which is soluble in cold water, and is believed to be the active principle.

ACTION OF NITRIC ACID ON ALOES.

When nitric acid is made to act on aloes with the aid of heat, a series of new compounds is formed, differing according to the concentration of the acid. Braconnot discovered one of these, namely *Polychromic acid;* and Schunck obtained, besides, two others, *Chrysammic acid* and *Chrysolepic acid.*

Polychromic acid: Syn. *Artificial bitter principle of aloes.*—To obtain this acid, 1 part of aloes is heated with 8 parts of nitric acid, sp. g. 1·25. When the reaction is over, the whole is evaporated to the consistence of syrup, and mixed with cold water, which throws down impure polychromic acid. It is purified by washing with water till the liquid passes through of a pure purple colour.

When pure, it forms a yellow or brown powder, of a bitter astringent taste, which is soluble in 800 parts of cold water, more easily in hot water. The solution is purple, and reddens litmus; it is turned yellow by acids. When heated, the powder explodes. The boiling solution gives to silk a deep purple colour; and, if different mordants be applied to the silk previously, it is dyed of all shades of brown, blue, violet, green and yellow, according to the mordant. All these colours resist the action of soap; but are bleached, sooner or later, by the action of light.

According to Schunck, polychromic acid is a mixture of two acids, Aloetic and Aloeresinic acids. The latter forms with most bases brownish red insoluble salts. The aloetic acid, on the contrary, forms salts, most of which are soluble. The aloetate of potash forms, when rapidly crystallised, small blood-red prisms; by spontaneous evaporation, long ruby-red needles. The composition of these acids is unknown.

Chrysammic acid.—Formula, $C_{15}HN_2O_{12} + HO$. (Schunck.) One part of aloes and 8 of nitric acid, sp. g. 1·37, are heated together, at first in an open vessel; and, when the first violent action is over, the whole is introduced into a retort, and distilled to two-thirds. More acid (about 4 parts) is then added, and the mixture kept at a heat near the boiling point for some days, as long as gas is disengaged. The greater part of the acid being distilled off, water is added, which throws down impure chrysammic acid, while chrysolepic and oxalic acids remain in solution.

The precipitated acid is purified by washing with water, which removes nitric, chrysolepic, and aloetic acids. It then forms a greenish yellow crystalline powder, which still contains aloeresinic acid. It is now combined with potash, and the salt purified by recrystallisation. The pure salt is dissolved in water; and, on the addition of nitric acid, pure chrysammic acid is deposited.

It forms a golden-yellow powder, composed of shining scales, soluble to some degree in hot water, forming a purple solution, which is bitter. It is easily soluble in alcohol, ether, and hot acids; and when heated it explodes. When heated in fuming nitric acid, it is decomposed, yielding a new compound in golden scales, which forms with potash an insoluble salt; with soda, one which crystallises in needles of a greenish golden colour.

When heated with oil of vitriol, chrysammic acid yields dark grey adamantine crystals, which are a new compound. This substance, when its solution is mixed with nitric acid, yields shining yellow scales, which are not chrysammic acid.

Chrysammate of potash forms, when crystallised out of a saturated boiling solution, a beautiful carmine-red crystalline powder; and, when more slowly produced, small greenish golden crystals, like those of murexide. The salts of soda and magnesia are similar.

With ammonia chrysammic acid forms a deep purple solution, which deposits dark green crystals. These are not chrysammate of ammonia, but probably an amide. If their solution be mixed with nitric acid, it becomes of a brighter colour, and on cooling deposits, not chrysammic acid, but black adamantine crystals, which, when boiled with potash, yield ammonia and are reconverted into chrysammic acid.

The other salts of this acid are of various shades of red, and all exhibit a golden lustre under the polishing steel.

Chrysolepic acid.—This acid is contained in the mother liquid and washings of the preceding. It is obtained by evaporation in crystals, which are purified by being combined with potash, and the salt recrystallised. The solution of the pure salt, treated with nitric acid, yields pure chrysolepic acid, in beautiful golden-yellow scales, of a darker colour than picric acid, which however it resembles in its properties. According to Schunck, its formula is $C_{12}H_2N_3O_{13}+HO$, being the same as that of picric acid, from which it is distinguished by its salts.

Chrysolepate of potash forms long shining yellow needles, which exhibit a violet metallic lustre by reflected light. *Chrysolepate of soda* forms long needles, which have a green metallic lustre. *Chrysolepate of silver* forms dark brownish red needles, which exhibit a play of red and green colours by reflected light.

A hot solution of the salt of potash or soda gives with acetate of lead yellow brilliant crystals, which are composed of basic chrysolepate and acetate of lead. These crystals dissolve in acetic acid; and the solution, when evaporated, deposits dark brown metallic-looking crystals, said to be neutral chrysolepate of potash. These characters serve to recognise the chrysolepic acid, and to prove that it differs from picric acid. The acid itself, and its salts, explode when heated, like picric acid and the picrates.

According to Boutin, when nitric acid and aloes are heated together in a retort, a volatile substance passes over, having the smell of bitter almonds. Its properties are unknown, and Schunck could not observe its presence in his experiments.

ASPARAGINE.

Syn. *Asparamide; Althéine; Agedoile.*—Formula of the crystals, $C_8H_8N_2O_6 + 2HO$; when dried at 248°, $C_8H_8N_2O_6$. It occurs in asparagus, in liquorice, in the root of *Althæa officinalis,* in *Symphytum tuberosum*, in the potato, and probably in many other plants.

It is obtained either by macerating althæa-root with milk of lime, precipitating the filtered liquor with carbonate of ammonia, and evaporating to the consistence of syrup; or by boiling the juice of asparagus, filtering and evaporation. It forms large transparent right rhombic prisms, or short six-sided prisms, of a cooling somewhat nauseous taste. It is soluble in water and weak spirits, insoluble in alcohol and ether. By the action of acids and alkalies, aided by heat, it is resolved into ammonia and *aspartic acid.*

Aspartic acid.—A bibasic acid. Formula of the hydrate, $C_8H_5NO_6 + 2HO$; of the anhydrous acid, $C_8H_5NO_6$.

Asparagine is boiled with aqua potassæ as long as ammonia is disengaged. The aspartate of potash is super-saturated with hydrochloric acid, and evaporated to dryness; cold water dissolves out the chloride of potassium, and leaves pure aspartic acid.

It forms delicate white micaceous scales of a pearly lustre, sparingly soluble in water, insoluble in strong alcohol. When boiled with strong potash, it is decomposed, yielding ammonia and a new acid, which is very soluble, but has not been studied.

It is derived from asparagine by the separation of 1 eq. ammonia, $C_8H_8N_2O_6 - NH_3 = C_8H_5NO_6$. The general formula of its salts is $C_8H_5NO_6 + 2MO$; but several exist of the formula $C_8H_5NO_6 + HO,MO$, as in other bibasic acids.

ORGANIC BASES OR ALKALIES.

The name of organic bases is applied, in the stricter sense, to a series of azotised compounds capable of forming salts with acids. They differ from the non-azotised bases, such as oxide of ethule, oxide of methule, &c. in this, that in their salts the acid may be transferred by double decomposition to other bases. In this respect the salts of the organic alkalies resemble those of ammonia.

Most of the organic bases are found ready formed in plants; these are called Vegetable bases. Others are formed in certain processes of decomposition. The name of Organic or Vegetable alkalies, or of Alkaloids, is given to those which in solution restore the blue of reddened litmus, or turn the yellow of turmeric to brown.

The first vegetable base was discovered by Sertuerner in 1804, and the number of them has very greatly increased since that time.

The general method of extracting them from the plant varies with the properties of the bases. When the base is insoluble in water, it is extracted by diluted acids, and the acid solution precipitated by an alkali. The same process applies where the insoluble base exists in the plant in the form of a soluble salt, which is extracted by water and decomposed by an alkali. The precipitated alkali is generally impure, and is purified either by crystallisation from alcohol, or by converting it into a salt, which, when purified by recrystallisation, yields the pure alkali on the addition of ammonia or some other base.

When the base is soluble, without being volatile, it is extracted by a dilute acid; and the concentrated solution is digested with potash and ether, which dissolves most or all of the vegetable bases of this class.

When it is soluble and volatile, the plant or its extract is distilled with potash, and yields a product containing the base with a mixture of ammonia. This is neutralised by oxalic or sulphuric acid, and evaporated to dryness. Alcohol now dissolves the sulphate or oxalate of the base, and this salt is agitated with potash and ether. The ether dissolves the base, and leaves it on being evaporated. The base is finally purified by distillation.

The alkaline character of the organic bases depends, in some way, on the nitrogen which they invariably contain. Many contain no oxygen; these are powerful bases: and, in contradistinction to the inorganic bases, those which contain oxygen neutralise less acid the more oxygen they contain. Most of them contain in 1 equivalent of the base 1 eq. of nitrogen; a few contain 2 or more equivalents of that element.

The organic bases, in the anhydrous state, combine directly with hydrogen acids.

Towards oxygen acids they behave like ammonia, combining only with the hydrated acids; and the hydratic water cannot be expelled from the salts without decomposition. Like ammonia, they form double salts with bichloride of platinum, when previously converted into hydrochlorates. They differ, however, from the ammoniacal salts in the amount of water of crystallisation present in their compounds with hydrochloric acid.

The salts of Aconitine, Atropine, Brucine, Cinchonine, Codeine, Conicine, Delphinine, Emetine, Morphine, Narcotine, Quinine, Strychnine, and Veratrine, are precipitated white by infusion of galls. The precipitate is a tannate, which, when exposed to the air, passes into a soluble gallate.

When exposed to the action of chlorine, the vegetable bases are decomposed, yielding hydrochloric acid, which combines with the undecomposed residue of the base. In solutions of their salts, chlorine produces various effects. Thus, solutions of brucine become yellow, orange, red, blood-red, and at last yellow again. In a solution of a salt of strychnine chlorine causes a white precipitate, even when only $\frac{1}{800}$th of strychnine is present. This precipitate contains chlorine and nitrogen. If brucine be present, it acquires a yellow or red colour. Solutions of cinchonine and quinine become yellow, rose-red, violet-red, and deposit a red resinous matter. Solutions of morphia become orange, blood-red, and lastly yellow, with a yellow precipitate. Narcotine becomes flesh-red, dark red, and finally deposits a brown powder. A solution of sulphate of quinine, saturated first with chlorine and then with ammonia, acquires a grass-green colour, and deposits a green powder.

When 2 parts of strychnine and 1 of iodine are dissolved in hot alcohol, there are deposited on cooling brilliant yellow scales, and the mother liquor gives crystals of hydriodate of strychnine. From a solution of brucine in alcohol, tincture of iodine precipitates a brownish orange powder. Quinine and cinchonine, treated in the same way, yield clear brown liquids, which on evaporation first deposit saffron-coloured scales of a new compound, and lastly hydriodate of the base.

These new compounds seem to be composed of iodine and the base. With acids, iodine is set free and the base remains dissolved. Their composition is not yet ascertained; and it is doubtful whether these compounds, described by Pelletier, are identical with those obtained by Bouchardat, by adding to the salts of organic bases a solution of ioduretted iodide of potassium.

When morphia is acted on by iodine, there are formed hydriodate of morphia and a brown compound which contains no morphia.

The action of acids on these bases is little known. Brucine and its salts are coloured red by nitric acid, also strychnine when it contains brucine. Morphia undergoes a similar change, and is also coloured brown by contact with a solution of iodic acid.

The action of alkalies on the organic bases has hardly been examined. According to Gerhardt, Quinine, Strychnine, Narcotine, and some other bases, when heated with caustic potash, yield oily liquids, which have alkaline properties. (See *Quinine.*)

In regard to the action of salts on the organic bases, we only know that morphia and its salts are coloured blue by the perchlorides of iron and gold. The blue colour is fugitive.

Such is a general account of this class of compounds. We shall consider them in the following order:

1. Volatile bases, containing no oxygen;

These are Aniline and Nicotine, to which may be added Conicine, although the absence of oxygen in this base is not certain.

2. Bases derived from oil of mustard;

These are Thiosinnamine, Sinnamine, and Sinapoline.

3. Bases of Cinchona bark;

These are Quinine, Cinchonine, and Aricine (?)

4. Bases of the Papaveraceæ;

These are Morphia, Codeine, Narcotine, Thebaine, Pseudomorphine, Narceine, and Chelidonine.

5. Bases found in the Solanaceæ, Strychnaceæ, and other plants;

These are Atropine, Solanine, Jervine, Brucine, Strychnine, Sabadilline, Veratrine, Delphine, Staphisine, Menispermine, Picrotoxine, Emetine, Corydaline, Berberine, Piperine, Harmaline, Caffeine, and Theobromine.

It should be observed, that, although their alkaline characters depend on the nitrogen they contain, it appears, from all experiments hitherto made, that this nitrogen is not present in the form of ammonia.

It is also important to notice, that the vegetable bases are either poisonous, or possessed of medicinal virtues; very commonly both. They are generally the active principles of the plants in which they occur.

The organic bases are often, for the sake of brevity, indicated, not by their formulæ, but by the initial letters of their names with the + sign over them. Thus the abbreviated symbol of morphia is $\overset{+}{M}$.

1. VOLATILE BASES.

Aniline: Syn. *Crystalline.* — Discovered by Unverdorben among the products of the distillation of Indigo; by Fritzsche as a product of the action of heat on Anthranilic acid. Formula, $C_{12}H_6N$. Symbol $= \overset{+}{A}$. In its formation, 1 at. anthranilic acid, $C_{14}H_6NO_4$, loses 2 at. carbonic acid, $= C_2O_4$, and aniline is left.

It forms a colourless oily liquid, which refracts light strongly, and has a strong unpleasant aromatic smell. It is sparingly soluble in water, miscible with alcohol and ether. It has decided alkaline characters, and forms with acids, such as hydrochloric and oxalic acids, salts which easily crystallise. It is gradually changed into a brown resinous substance by exposure to the air.

Nicotine.—Discovered in Tobacco by Reimann and Posselt. Formula, $C_{10}H_8N$. Symbol, $\overset{+}{N}$. It is obtained by the general process above described for soluble and volatile bases. It forms a colourless clear oily liquid, which has a weak odour of tobacco, except when ammonia is present, in which case the smell is powerful. It boils at 585°, but is decomposed; it distils slowly, however, at a lower temperature. Its sp. g. is 1·048. It has a distinct alkaline reaction, is miscible with water, and separates when the solution is saturated with hydrate of potash. It is very soluble in alcohol, ether, and oils. It is decomposed by exposure to air, and the action of chlorine, iodine, and nitric acid.

Nicotine is a frightful poison; one-fourth of a drop will kill a rabbit, one drop a dog. It does not dilate the pupil. It combines with and neutralises acids, forming salts which are very soluble in water and alcohol, and crystallise with difficulty. Hydrochlorate of nicotine gives with bichloride of platinum a sparingly soluble and crystallisable double salt, which is slowly deposited in large orange-red prisms. If ammonia be present, the platinochloride of ammonium is instantly precipitated, and the filtered liquid on standing deposits the double salt of nicotine pure. Formula of this salt, $C_{10}H_8N,HCl + PtCl_2$.

A solution of nicotine in water gives with corrosive sublimate a white precipitate, the formula of which seems to be $2(C_{10}H_8N) + HgCl_2$. For the analysis, both of nicotine and of the two compounds just described, we are indebted to Ortigosa.

When nicotine is digested with fused potash, it yields two strata of liquid. The upper contains much potash, and, when distilled, yields an oily fluid of an agreeable odour, which forms with bichloride of platinum a very soluble salt in yellow scales, and is therefore distinct from nicotine.

Conicine: Syn. *Conia; Cicutine.*—Discovered by Gieseke, but first obtained pure by Geiger. Occurs in *Conium maculatum.* Formula, $C_{12}H_{14}NO$ (?). Symbol, $\overset{+}{Co}$.

It is best obtained from the seeds by distillation with water and potash, and is purified in the manner recommended above for volatile bases. When pure, it forms a transparent colourless oily liquid, sp. g. 0·89. It has a pungent and nauseous smell, which is stupifying and excites a flow of tears, and an acrid pungent nauseous taste. It is a most active poison, since from one-eighth of a grain to one grain will destroy a small animal, death being preceded by rigid cramps. It does not enlarge the pupil. In the hydrated state it has a powerful alkaline reaction. It boils at 338°, but distils at a much lower temperature when water is present. It is partially decomposed when heated in contact with air, ammonia being produced. It is also decomposed by all the strong mineral acids, by chlorine and by iodine, yielding a great variety of colours, some of them beautiful.

Conicine is more soluble in cold than in hot water; and water also is more soluble in conicine when cold than when heated. It is easily miscible with alcohol and ether. It neutralises acids completely; and its salts are very soluble, crystallising with difficulty. Their solutions are easily decomposed, and the conicine gradually disappears, yielding ammonia and a bitter extractive matter which is not poisonous. The hydrochlorate forms *in vacuo* large foliated crystals which are deliquescent. Its solution, when evaporated in air, becomes first purple, then deep blue.

From the facility with which conicine is decomposed in the plant or its extract, the pharmaceutical preparations of hemlock are most uncertain in their activity. Hence pure conicine ought to be used, as it is uniform and may be preserved without difficulty.

It is not yet ascertained whether oxygen be an essential ingredient of conicine.

2. BASES FROM OIL OF MUSTARD.

Thiosinnamine.—When the oil of mustard is brought in contact with three or four times its volume of strong ammonia, crystals are formed, which are purified by recrystallisation. These are Thiosinnamine. Formula, $C_8H_8N_2S_2$. (Varrentrapp and Will.)

Thiosinnamine is soluble in hot water, less so in cold water, soluble in alcohol and ether. It has a bitter taste and no smell. At 392° it is resolved into ammonia and a resinoid basic compound not fully investigated. Thiosinnamine combines with acids, but its salts do not crystallise: it yields a double salt with chloride of platinum, $C_8H_8N_2S_2,HCl + PtCl_2$; and a compound with corrosive sublimate, which is $C_4H_4NS + HgCl_2$.

Sinnamine.—Obtained by digesting thiosinnamine with moist hydrated protoxide of lead till all the sulphur is removed. The mass is then extracted by water, finally by alcohol, and the liquors evaporated to a syrup, which after some time deposits fine transparent crystals of sinnamine.

Sinnamine is a powerful base, expels ammonia from its salts, and precipitates the solutions of peroxide of iron, of copper, and of lead. It combines with acids, but yields no crystallisable salts. It precipitates the bichlorides of platinum and mercury, and nitrate of silver. When heated, it gives off ammonia, and leaves a resinoid matter which is also basic. The production of sinnamine from thiosinnamine is easily explained, as it is formed by the separation of all the sulphur and an equivalent amount of hydrogen. Thus $C_8H_8N_2S_2 + 2PbO = C_8H_6N_2 + 2PbS + 2HO$. It is not known with certainty whether the formula of sinnamine is $C_8H_6N_2$ or C_4H_3N. (Varrentrapp and Will.)

Sinapoline.—This compound, discovered by Simon, is obtained by depriving oil of mustard of its sulphur by the action of baryta or of oxide of lead. It is soluble in hot water and alcohol, and crystallises in shining, fatty, fusible scales. Its solution has an alkaline reaction. It combines with acids, and is separated from them by ammonia. It also precipitates, when combined with hydrochloric acid, the bichlorides of platinum and mercury.

It is formed from oil of mustard by the subtraction of 2 at. of bisulphuret of carbon, and the addition of 2 at. of water. Thus, $C_{16}H_{10}N_2S_4 + 2HO = C_{14}H_{12}N_2O_2 + 2CS_2$. Formula of sinapoline, $C_{14}H_{12}N_2O_2$.

3. BASES OF CINCHONA BARK.

Quinine: Syn. *Chinine.* — Formula, $C_{20}H_{12}NO_2$. (Liebig.) Symbol $\overset{+}{Q}$. Discovered, along with cinchonine, by Pelletier and Caventou. Occurs in all genuine cinchona bark, but in greatest abundance in *Cinchona regia vera*, or *Calisaya*, and in the yellow bark, *C. cordifolia.* The bark is exhausted, in an apparatus of displacement, by a dilute acid, the solution boiled with milk of lime, and the precipitate, when boiled with alcohol, yields quinine, generally mixed with cinchonine. The latter crystallises readily, and the mother liquor retains the quinine. Ether dissolves quinine from the dried residue, and leaves any cinchonine that may be present.

Quinine may be obtained in crystals from its solution in very strong alcohol by spontaneous evaporation, also from its solution in hot water with a little ammonia, in fine silky needles. It commonly occurs as a porous dirty white resinoid mass. The crystals are a hydrate. It is sparingly soluble in cold water, rather more so with the aid of heat, and the solution has an alkaline reaction. It is also soluble in alcohol and ether. Its solutions are bitter.

With acids it forms crystallisable salts, soluble in water and alcohol. Solutions of these salts give with alkalies a flocculent white precipitate of quinine; and with tincture of galls a white precipitate. The most important of these salts is the sulphate, which is very extensively employed in medicine. Various processes are given for its preparation; but the essential part of all of them is to dissolve the impure quinine in dilute sulphuric acid, avoiding excess of acid, to digest the solution with animal charcoal, and to evaporate. The salt then forms fine light feathery crystals, which are snow-white. The sulphate of commerce is a basic salt, $2\overset{+}{Q} + SO_3 + 8HO$; and is preferred on account of its sparing solubility in cold water, which prevents material loss in its preparation. The neutral sulphate is much more soluble, and forms small needles. Other salts, such as the phosphate, acetate, hydrochlorate, citrate, ferrocyanate, kinate, &c. have been recommended for medical use. They are all very bitter to the taste.

The salts of quinine are often adulterated with gypsum, chalk, magnesia, boracic acid, sugar, mannite, starch, stearic acid, or salicine. Alcohol leaves the three first undissolved. If boracic acid be present, the alcohol will burn with a green flame. Sugar and mannite are extracted by cold water; and stearic acid is left undissolved by hot diluted acids. Starch is detected by iodine; and, if salicine be the contamination, it is turned red by sulphuric acid. Salicine and cinchonine, however, if present, do not affect the medicinal virtue of the salts of quinine.

Gerhardt has recently stated, (Ann. der Chem. und Phys. xlii. 310,) that, when quinine is distilled with potash and a little water, it yields an oily liquid, of basic properties, which he calls *Chinoiline*, while hydrogen is given off.

It unites with acids, neutralising them, and forming crystallisable salts. It also forms, when combined with hydrochloric acid, and mixed with bichloride of platinum, a beautiful double salt, the formula of which is $C_{18}H_{11}NO_2, HCl + PtCl_2$. From this, Gerhardt deduces the formula $C_{18}N_{11}NO_2$ for chinoiline. If this be correct, and if the formula of quinine be $C_{20}H_{12}NO_2$, then quinine loses by oxidation 2 at. of carbon and 1 of hydrogen to yield the new base. Gerhardt assumes for quinine the formula $C_{38}H_{22}N_2O_4$, which, losing 2 at. of carbon by oxidation, would give $C_{36}H_{22}N_2O_4 = 2(C_{18}H_{11}NO_2)$.

It is probable that this method of decomposition, which appears to be applicable to other vegetable alkalies, may materially assist in clearing up the history and fixing the composition of this class of compounds.

Cinchonine is found in greatest abundance in the red bark, *C. oblongifolia*, and the pale bark, *C. condaminea*. In the former it is associated with much quinine; in the latter with very little or none. It is also found in yellow bark in smaller quantity than quinine. Formula, $C_{20}H_{12}NO$; symbol $\overset{+}{\mathrm{Ci}}$.

The method of preparing it is the same as for quinine; and the alcoholic solution of the precipitate caused by alkalies deposits cinchonine in crystals by evaporation, while the quinine remains dissolved. Cinchonine forms large brilliant prisms, which may be volatilised by heat carefully applied. It is very insoluble in water, also in ether; soluble in strong alcohol.

It neutralises acids, forming crystallisable salts, more soluble than those of quinine and very bitter. Their solutions are precipitated white by alkalies and by tincture of galls. The sulphate may be employed for the same purposes as that of quinine.

It is to be observed, that the formula of quinine and cinchonine differ only by 1 atom of oxygen; and it is probable that one may be derived from the other, although this has not been proved experimentally.

Chinoidine.—This name has been given to a substance found in the mother liquors of quinine and cinchonine, which has been described by several chemists as a new alkali. Its physical properties, however, render this doubtful, as it is resinous and coloured. The chinoidine of some chemists has been resolved into quinine, cinchonine, and a resinous matter by others; but, as the saturating power of chinoidine is said to be greater than that of quinine, future experiments must decide the question of its separate existence. In the mean time the so-called chinoidine is used as a cure for intermittents, and is said to be very effectual.

Aricine.—This name has been given by Pelletier to an alkali discovered by him in the *Cusco bark* or *Arica bark.* It is said to contain 1 atom of oxygen more than quinine; so that quinine, cinchonine, and aricine would be three oxides of the same radical. This, as well as the existence of aricine, requires confirmation. Nothing is known of its action on the system.

Several other alkalies are said to have been discovered in different varieties of cinchona bark, but their existence is doubtful.

4. BASES OF THE PAPAVERACEÆ.

Morphia or *Morphine.*—Formula, $C_{35}H_{20}NO_6$; symbol, $\overset{+}{M}$. Discovered by Sertuerner, 1804. The easiest method of preparing it is the following, proposed by Gregory and Robertson. An infusion of opium in cold water is concentrated, and heated with chloride of calcium in solution. The precipitate of meconate of lime, which separates, is removed by filtration, and the filtered liquid evaporated to the consistence of thin syrup. On standing, the liquid becomes nearly solid by the separation of hydrochlorate of morphia, which is purified by expressing the dark mother liquor, and recrystallising the salt, with the aid of animal charcoal. When the hydrochlorate is quite white, which may require from 2 to

4 crystallisations, according to the power of the press employed, it is dissolved in hot water, and supersaturated with ammonia, when the morphia falls as a snow-white, crystalline powder. (From the mother liquid codeine is obtained. — See *Codeine*.) Many other processes have been given; but although some of them, in which alcohol is used, may answer well where that solvent is cheap, the above process, according to the experience of the Edinburgh manufacturers, is the easiest and the most productive, especially on a large scale. Good opium yields from 10 to 13 per cent. of morphia.

Merck precipitates the infusion of opium with carbonate of soda in excess, washes the precipitate with cold water and cold alcohol of sp. g. 0·85, and dissolves the residue in weak acetic acid, from which, after filtering through charcoal, the morphia is precipitated by ammonia. It is finally crystallised from hot alcohol. This is an excellent process where alcohol is cheap.

Mohr adds the infusion to a milk of lime containing lime equal to one-fourth to one-sixth of the weight of the opium, boils for a short time and filters while hot. The excess of lime dissolves the morphia, forming a wine-yellow solution, which is evaporated till it is double the weight of the opium, and then heated with powdered sal-ammoniac, one ounce being added for one pound of opium. On cooling, the morphia is deposited in coloured crystals, which are purified by a second solution in lime and precipitation by sal-ammoniac. This is also a good process, and is the best for operating on a small scale, as in testing the quality of opium.

Morphia forms, when crystallised from alcohol, brilliant colourless prisms of adamantine lustre. The crystals contain 2 atoms of water, which are expelled by heat. It is fusible and is destroyed by a high temperature. Nitric acid colours it orange-red; iodic acid, brown, iodine being set free; and perchloride of iron, blue, which last colour is very fugitive.

It is very sparingly soluble in water; soluble in alcohol, especially with the aid of heat; insoluble in ether. Its alcoholic solution is very bitter. It likewise dissolves readily in the fixed alkalies and in lime. From the above characters, its purity is easily ascertained.

Morphia is the chief active principle of opium. In small doses it is powerfully anodyne; in large doses it causes death with narcotic symptoms. It is less active in the uncombined state than in the form of a salt, owing to its sparing solubility.

It neutralises acids, forming crystallisable salts, of which the hydrochlorate, acetate, and sulphate are most employed. The preparation of the hydrochlorate has been described; but the commercial salt thus prepared generally contains about one-thirtieth of codeine. The pure hydrochlorate, as well as the acetate and sulphate, may be best prepared by dissolving pure morphia in the acids, and crystallising. These salts form delicate feathery masses of fine crystals, similar to sulphate of quinine. They are generally sold in powder. Nitric and iodic acids and perchloride of iron act on them as on pure morphia. They are all easily soluble in alcohol. A solution of any of these salts, 5 grains to the ounce of water, forms an admirable substitute for laudanum, and is of the same strength. Ten grains of hydrochlorate of morphia have proved fatal; and probably half that quantity, or even less, would do so. It is very difficult to detect morphia or its salts after death, as they are rapidly removed from the stomach by absorption. Where opium or laudanum has been the cause of death, it is more easy to detect the meconic acid they contain, by its action on the salts of peroxide of iron.

Codeine.—Discovered by Robiquet in repeating the process of Gregory and Robertson above described. Formula, $C_{35}H_{20}NO_5$; symbol, $\overset{+}{Cd}$.

When the purified commercial hydrochlorate of morphia is precipitated by ammonia, the mother liquor on evaporation yields a salt exactly like the hydrochlorate of morphia; but which is a double salt, composed of the hydrochlorates of morphia and codeine. It is digested with aqua potassæ, which dissolves the morphia, and leaves the codeine as an oily viscid mass, which, on cooling, consolidates into crystals. It is farther purified by ether, in which it dissolves; and by the addition of a little water, and spontaneous evaporation, it crystallises in a state of purity.

Codeine is soluble in water, alcohol, and ether. Its aqueous solution deposits by slow evaporation very large transparent octohedrons. These, when heated, melt, and lose their water of crystallisation. It has a bitter taste and is decidedly alkaline. It is not coloured by nitric acid, nor by perchloride of iron. It is insoluble in alkalies.

Codeine neutralises acids and forms crystallisable salts, such as nitrate, sulphate, and hydrochlorate.

It seems to possess anodyne properties; and its salts often cause general and violent itching of the skin. (Gregory.) Perhaps codeine is the cause of the itching which often follows the use of opium and of the common hydrochlorate of morphia, which latter salt contains one-thirtieth of codeine. The pure hydrochlorate of morphia is said not to produce this effect. (Gregory.) As codeine is almost invariably present in opium, its action on the system deserves to be minutely investigated.

As an additional distinction of codeine from morphia, it may be added, that tincture of galls precipitates the salts of codeine abundantly, but does not act on those of morphia.

It is also to be remarked that the relation between the formulæ of codeine and morphia is the same as between those of cinchonine and quinine, the morphia containing 1 atom of oxygen more than the codeine.

Thebaine: Syn. *Paramorphine.*—Discovered by Thiboumery. Formula, $C_{25}H_{14}NO_3$. (Kane.)

When an infusion of opium is acted on by excess of lime, the morphia is dissolved; and the residue yields, when dissolved in diluted acid and precipitated by ammonia, a powder, which, when dissolved in alcohol or ether, leaves thebaine on evaporation.

It forms colourless crystals, has a sharp metallic taste and an alkaline reaction. It is fusible. It combines with diluted acids, forming crystallisable salts. Its action on the system is unknown, and its formula is not ascertained with certainty.

Pseudomorphine.—Discovered by Pelletier, who, however, has only found it in two specimens of opium. Formula, $C_{27}H_{18}NO_{14}$?

It is sparingly soluble in water, insoluble in alcohol and ether, soluble in alkalies. It forms shining scales. It dissolves readily in acetic and hydrochloric acids, but its salts have not been studied. Like morphia, it is coloured blue by the salts of peroxide of iron.

Narceine.—Discovered by Pelletier. Occurs also in opium. Formula, $C_{28}H_{20}NO_{12}$? (Couerbe); or $C_{32}H_{24}NO_{16}$? (Pelletier). It is extracted from the brown mother liquors of morphia or hydrochlorate of morphia by a tedious process. It is sparingly soluble in water, very soluble in alcohol, insoluble in ether, and may thus be purified from the other ingredients of opium. It forms fine silky crystals, which have a metallic taste. It dissolves in diluted acids without neutralising them, and the solutions on evaporation deposit unaltered narceine. It is coloured blue by strong acids (yellow by nitric acid) and by substances having a strong attraction for water, such as chloride of calcium, but not by the salts of iron.

Narcotine.—Discovered by Derosne. Formula, $C_{40}H_{20}NO_{12}$? or $C_{48}H_{24}NO_{15}$?

Narcotine occurs also in opium, and is best obtained by extracting the residue, left by cold water, with acetic acid. The addition of ammonia causes a precipitate, which is dissolved in hot alcohol, decolorised by animal charcoal, and crystallises on cooling.

It forms colourless shining needles, which are fusible. It is insoluble in water, soluble in alcohol and ether, insoluble in alkalies. Its solutions are very bitter. It is turned blue by the salts of peroxide of iron, and is not reddened by nitric acid; but sulphuric acid, containing a trace of nitric, tinges it blood-red.

It combines with acids, and some of its salts have been crystallised; but they have always an acid reaction. It is very doubtful whether narcotine or its salts, when free from morphia, &c., have any action on the system.

When, as often happens, morphia is contaminated with narcotine, it is separated, either by alkalies such as potash or lime, which dissolve the morphia and leave the narcotine, or by converting the mixture into a hydrochlorate and crystallising. The whole of the narcotine remains in the mother liquor.

Chelidonine.—Discovered by Godefroy; studied by Polex, Probst, and Reuling. Occurs in *Chelidonium majus*, and in *Glaucium luteum.* Formula, $C_{40}H_{20}N_3O_6$. (Will.)

When pure, it forms colourless scales, of a bitter taste, insoluble in water, soluble in alcohol and ether. It forms with acids crystallisable salts, which have an acid reaction. Their action on the system has not been investigated.

From the same plants, Chelidonium majus and Glaucium luteum, Probst obtained another base, which he calls Chelerythrine. When pure, it forms a grey powder, which powerfully excites sneezing. It is insoluble in water, soluble in alcohol. Acids give it a fine orange-colour, and form with it coloured salts, which are neutral, and act as narcotics in a small dose. Some of these salts have been crystallised.

In *Glaucium luteum* Probst has, moreover, discovered two other bases, Glaucine and Glaucopicrine. *Glaucine* forms pearly scales, which are soluble in hot water, in alcohol, and in ether. It is easily fusible; and forms with acids neutral salts, which are colourless, crystallisable, and have an acrid taste. When heated with oil of vitriol in an open vessel, it yields an indigo-blue product.

Glaucopicrine forms white scales, soluble in hot water, ether, and alcohol. It has a bitter taste, neutralises the acids perfectly, and forms colourless crystallisable salts, which have a bitter and nauseous taste. When heated with oil of vitriol, it yields a dark green, tough mass.

5. BASES FOUND IN THE SOLANACEÆ, STRYCHNACEÆ, AND OTHER NATURAL FAMILIES.

Hyoscyamine.—Discovered by Geiger and Hesse in *Hyoscyamus niger;* occurs probably also in *H. albus.* Its formula is unknown.

It is purified by a tedious and difficult process, and much is lost in the various operations. It may be obtained in crystals, but is commonly got as a viscid mass. When moist, it has a strong alkaline reaction, and a penetrating, narcotic, and stupifying odour, like that of nicotine. It is equally poisonous with nicotine, and produces the same symptoms, except that it enlarges the pupil strongly and permanently. It may be distilled, but is partially decomposed by heat; and it is rapidly destroyed by contact with alkalies. It is somewhat soluble in water, very soluble in alcohol and ether.

It neutralises acids, forming salts, some of which crystallise, and all of which are poisonous. Hyoscyamine and its salts should be employed in medicine, as being more uniform in activity than the plant, or its extract, tincture, &c.

Daturine.—Discovered by Geiger and Hesse in *Datura Stramonium.* It probably occurs in other species of Datura. Its formula is not ascertained.

It is best obtained from the seeds, by a method similar to that for hyoscyamine. It forms large brilliant prisms, in radiated groups. It is sparingly soluble in cold water; more so in hot water, alcohol, and ether. When impure and moist, it has a nauseous narcotic odour. Its taste is at first bitter, then acrid; and it is as poisonous as hyoscyamine, dilating the pupil strongly. It may be sublimed unaltered, and is altogether less easily decomposed than hyoscyamine. Its solution in alcohol crystallises with difficulty; but, if water be added, it yields fine prisms.

Daturine neutralises acids and forms crystallisable salts, which have been little examined. Daturine and its salts deserve a trial as remedies.

Stramonine.—Found by Trommsdorff accompanying daturine. It crystallises in needles, is insoluble in water, sparingly soluble in alcohol, very soluble in ether. It has neither taste nor smell; and may be sublimed, if cautiously heated. It is as yet little known.

Atropine.—Discovered by Mein, Geiger, and Hesse in *Atropa Belladonna.* Formula, $C_{34}H_{23}NO_6$? (Liebig.) It is best obtained from the root, by a tedious process, analogous to those above described.

It crystallises in small white prisms, which are soluble in water and alcohol. The solutions, when heated, are easily decomposed. It neutralises acids, and forms salts, which are also easily decomposed; ammonia being one of the products.

It is a most energetic poison; and the smallest portion of it, or of any of its salts, produces great and permanent dilatation of the pupil. The extract of Belladonna is much used in diseases of the eye; but is very variable in its activity, and sometimes inert. Atropine and its salts would of course, if pure, be uniform in their effects.

Solanine occurs in several species of *Solanum*, and is found in considerable quantity in the shoots of potatoes which have germinated in a dark cellar. (Otto.) Formula, $C_{84}H_{68}NO_{28}$? (Blanchet.)

To obtain it, the shoots are bruised, and extracted by water acidulated with sulphuric acid. The filtered solution is precipitated while hot with an excess of ammonia; and the precipitate, collected on a filter, washed with ammonia till the liquid passes through colourless, dried, and boiled with alcohol. The solution, filtered while hot, deposits on cooling a large quantity of pure solanine in light feathery crystals of a pearly lustre. (Otto; Reuling.)

Solanine is insoluble in water, soluble in hot alcohol. It neutralises acids, forming crystallisable salts, which have an acrid taste. It is very poisonous. Its true formula is still doubtful.

Veratrine occurs in *Veratrum album* and *V. Sabadilla.* Formula, $C_{34}H_{22\frac{1}{2}}NO_6$? (Couerbe.)

This alkali occurs in the form of a powder, which is hardly crystalline, and is probably not yet known in a state of purity. On this account its chemical history is very imperfect. It is insoluble in water, soluble in alcohol and acids, and has a very acrid taste. It is a powerful poison, and has been much employed as a remedy, chiefly externally, in tic-douloureux, rheumatism, sciatica, &c. Dr. Turnbull of London has used it with great success, and has published an account of his experiments. The powder applied to the nostril causes violent and dangerous sneezing.

Jervine.—Discovered by Simon in *Veratrum album* along with veratrine. Formula, $C_{60}H_{45}N_2O_5$. (Will.) It is white and crystalline, fusible, insoluble in water, soluble in alcohol. It forms with acetic acid a soluble salt; but, with sulphuric, nitric, and hydrochloric acids, salts which are very sparingly soluble in water. This property enables us to separate it from veratrine. Its action on the system is unknown.

Sabadilline.—Discovered by Couerbe in *Veratrum Sabadilla.* Formula, $C_{20}H_{12\frac{1}{2}}NO_5$? (Couerbe.) Of its chemical history and medicinal properties very little is known; and the formula above given, like that of veratrine, is doubtful.

Strychnia.—Discovered by Pelletier and Caventou in several species of Strychnos, such as *Strychnos Nux vomica*, *S. colubrina*, and *S. Ignatii.* The latter contains most, but it is generally obtained from the more abundant Nux vomica. Formula, $C_{44}H_{23}N_2O_4$; symbol, $\overset{+}{\mathrm{St}}$.

The process for preparing it is analogous to those for morphia and quinine. The alcoholic or aqueous extract is precipitated by lime, and the precipitate boiled with alcohol, which on cooling deposits impure strychnia. It is accompanied with brucia, which is separated by combining both with dilute nitric acid, and crystallising. The nitrate of strychnia crystallises readily, while that of brucia remains in the mother liquid. From the pure nitrate the strychnia is precipitated by ammonia.

It forms a white powder, which requires about 7000 parts of cold water for solution, and gives to the water a most intense and persistent bitter taste. It dissolves in hot alcohol, sp. g. 0·850, and on cooling is deposited in brilliant, colourless, transparent thick prisms or octohedrons. It is hardly soluble in absolute alcohol, and insoluble in ether. It is an energetic poison, acting on the nervous system, and producing tetanus. It is much employed as a remedy in paralysis, especially when partial.

Strychnia unites with acids, neutralising them, and forming crystallisable salts. When pure, strychnia and its salts are not reddened by nitric acid; but when brucia is present, as in commercial strychnia, this effect is produced.

Brucine.—Discovered by Pelletier and Caventou in *Brucea antidysenterica*, and afterwards as accompanying strychnia in Nux vomica. Formula, $C_{44}H_{25}N_2O_7$. It would appear to be closely related to strychnia, containing 2 at. of water and 1 of oxygen more than that base, and therefore to bear to it the same relation as quinine to cinchonine or morphia to codeine.

Brucine neutralises acids, forming crystallisable salts. It is soluble in water to a certain extent, very soluble in alcohol. It is strongly reddened by nitric acid. It has a very bitter taste; and its action on the system is the same as that of strychnia, only much less energetic. Hence the presence of a little brucine in the strychnia of commerce is not injurious.

Delphine occurs in *Delphinium Staphysagria*. Formula, $C_{27}H_{19}NO_2$? (Couerbe.) It is obtained as a powder analogous in its characters to veratrine, and has been employed with almost equal success by Dr. Turnbull.

Staphysine accompanies delphine. Formula, $C_{32}H_{23}NO_2$? (Couerbe.)

Aconitine.—Discovered by Geiger and Hesse in *Aconitum Napellus* and *A. ferox*. Our knowledge of this base is very limited There is reason to think, from the experiments of Dr. Turnbull either that the plant contains two bases, or that the aconitine of Geiger and Hesse is an altered product. Dr. Turnbull has succeeded in producing, but with difficulty and in small quantity, an aconitine possessing inperfection all the active properties of the plant. It produces numbness of the tongue when applied to it, and is said to contract the pupil, whereas Geiger's aconitine dilates it. In obtaining the aconitine of Turnbull much appears to depend on the freshness of the plant; and the alkaloid itself is easily decomposed, especially by alkalies.

As a remedy in neuralgia and similar painful and obscure diseases, the aconitine of Turnbull possesses most valuable powers. Could it be obtained at a reasonable price, it would be extensively employed. At present, however, only one manufacturer has been able to obtain it, and that in small quantity. The aconitine of Geiger and Hesse does not appear to possess the same action on the system.

Picrotoxine.—Discovered by Boullay in Cocculus Indicus, the seeds of *Menispermum cocculus;* and examined by Pelletier, Couerbe, and Regnault. These chemists stated that it contained no nitrogen; but the recent researches of Francis have shown that, like other vegetable bases, it is azotised. Its true formula has not yet been published by the latter chemist, but he found in it 1·38 per cent. of nitrogen.

It forms colourless prisms, which have an intensely bitter taste. It is soluble in hot water, and in alcohol. Its basic properties appear to be feeble. It is very poisonous.

Menispermine.—Discovered by Pelletier and Couerbe in Cocculus Indicus. Formula, $C_{18}H_{12}NO_2$?

Paramenispermine. — Said by the same chemists to accompany the preceding, and to have the same composition, but different properties.

Emetine is the emetic principle of *Cephaelis ipecacuanha.* It is a white powder, slightly bitter, fusible, sparingly soluble in water, very soluble in alcohol. Formula, $C_{37}H_{27}NO_{10}$? (Pelletier.)

Harmaline.—Discovered by Göbel in the seeds of *Peganum Harmala.* Formula, $C_{24}H_{13}N_2O$. (Varrentrapp and Will.)

It forms yellowish brown crystals, of a bitter astringent and acrid taste, sparingly soluble in water and ether, more soluble in alcohol.

It is basic, and forms with acids yellow soluble salts, some of which crystallise. Harmaline may be used as a yellow dye; and by oxidation may be made to yield a magnificent red dye-stuff, which is likely to be much employed, as the seeds are produced abundantly in southern Russia, and the preparation and application of the colouring matter, according to Göbel, are very easy.

Piperine occurs in both white and black pepper. Formula, $C_{34}H_{19}NO_6$. (Regnault.) It is commonly considered as neutral; but, according to Varrentrapp and Will, it combines, like the vegetable alkalies, with hydrochloric acid gas, forming a salt which unites with bichloride of platinum. The hydrochlorate of piperine is decomposed by water.

Piperine forms rhomboidal prisms, which are colourless, tasteless, and inodorous; fusible, not volatile. It is nearly insoluble in water, soluble in alcohol, and with oil of vitriol gives a red colour.

Berberine.—Discovered by Buchner in *Berberis vulgaris.* Formula, $C_{33}H_{18}NO_{12}$. It forms a bright yellow crystalline powder, of a silky lustre, which has a strong bitter taste. It is sparingly soluble in cold water, but tinges it strongly yellow. It dissolves more easily in boiling water and alcohol, and is deposited in crystals on cooling. It is insoluble in ether.

It is decomposed by strong acids, and sparingly dissolved by dilute acids. Alkalies colour it brown, and it combines with several metallic oxides. It forms an insoluble compound with tannic acid. Its basic characters are very indistinct, and it would rather appear to belong to the class of azotised colouring matters.

Corydaline occurs in the root of *Corydalis bulbosa*, and *C. fabacea.* Formula, $C_{34}H_{22}NO_{10\frac{1}{2}}$? (F. Dœbereiner.)

Caffeine : Syn. *Theine ; Guaranine.*—Discovered by Pfaff in coffee. Occurs also in tea, (*Thea viridis* or *T. bohea,*) and in *Guarana officinalis.* Caffeine, theine, and guaranine, at first described as distinct compounds, have recently been proved to be identical. Formula, $C_8H_5N_2O_2$. (Pfaff and Liebig; Jobst ; Martius.)

Caffeine forms silky white needles, sparingly soluble in cold water and alcohol, easily with the aid of heat. It crystallises readily from an infusion of raw coffee, when certain impurities have been removed by subacetate of lead, and the excess of lead by sulphuretted hydrogen. It has a mild bitter taste.

With sulphuric and hydrochloric acids it forms crystallisable compounds. The latter yields large and beautiful crystals.

Although caffeine has no poisonous properties, and does not exhibit a marked action on the system, it is yet highly probable that it produces important effects. In addition to the remarkable fact, that it is found in tea and coffee, both of which are used by whole nations as a refreshment, Liebig, in his late work on Animal Chemistry and Physiology, has shown that the composition of caffeine is closely related to that of taurine, one of the ingredients of bile (see *Bile*) ; and that there is reason to believe that it may assist in the production of bile, and thus facilitate the process of respiration.

Theobromine.—Discovered by Woskresensky in the seed of *Theobroma cacao,* which yields chocolate and cocoa. Formula, $C_9H_5N_3O_2$, or $C_{18}H_{10}N_6O_4$.

It is very similar to caffeine, having the same taste; but is almost insoluble in water, alcohol, and ether. It is remarkable for the large proportion of nitrogen it contains, about 35·4 per cent.

It not only occurs in a substance which is used with the same intention as tea and coffee, for the sake, namely, of its power in refreshing and gently stimulating the system; but has also been shown by Liebig to be closely related, as caffeine is, to taurine, and moreover to urea and uric acid. This renders the opinion still more probable that caffeine and theobromine contribute to the formation of bile, with which that of urine is connected, and aid the process of respiration.

A number of substances have been named and described as vegetable alkalies, the true history of which is so little known that it is at present unnecessary even to give a list of them. Many are probably neutral, and identical with some of the neutral vegetable products formerly described. Others will perhaps be found to be identical with known alkalies. In all cases, further experiments are wanting.

NEUTRAL OR INDIFFERENT COMPOUNDS WHICH OCCUR GENERALLY IN VEGETABLES.

Under this head we have to consider certain substances, namely, starch, gum, and woody fibre, which are found in every plant, and constitute the principal mass of the vegetable kingdom.

Starch: Syn. *Fecula; Amylon.*—Formula of starch dried at the ordinary temperature, $C_{12}H_9O_9,HO + 2aq$. Dried at 212°, $C_{12}H_9O_9,HO$. Formula of its compound with oxide of lead, $C_{12}H_9O_9,2PbO$. (Payen.)

Starch occurs abundantly in the seeds of the cerealia; in many roots, such as the potato, and arrow-root, the root of *Maranatha arundinacea;* in the stems of many monocotyledonous plants, such as palms; and in several lichens. It is also found, according to Liebig, in unripe apples and pears, and in the seeds of leguminous plants. It is most easily obtained pure from potatoes.

Starch forms small rounded brilliant grains, varying in size from $\frac{1}{200}$th to $\frac{1}{10000}$th of an inch in diameter. These are composed of concentric layers or membranes, of which the outer one is thickest. When starch is dried at 140°, it forms translucent grains of a larger size formed by the rapid drying of the jelly which it forms with water. This is the case with sago and tapioca, which are nearly pure starch:

the former from the pith of a palm, *Sagus Rumphii;* the latter from the juice of *Iatropha Manihot*, which, although poisonous, deposits on standing a powder which is inert, being starch.

The starch of wheat-flour is contaminated with gluten, which is removed by fermentation, an acid being produced; or, still better, by the action of a weak alkaline solution.

Starch, when pressed in the fingers, gives out a peculiar sound. It is insoluble in cold water, but dissolved by hot water into a stiff jelly, which is much used for stiffening linen. It is dissolved by diluted acids; and, when this solution is boiled, it undergoes a remarkable series of changes. Thus, pure starch is coloured blue by iodine. When its solution in diluted acids has been boiled for some time, it is coloured purple by iodine; and, after a still longer interval, iodine ceases to colour it. In the latter case, the starch is found to be converted into a substance soluble in cold water, and having most of the properties of gum. This is called *Dextrine*, and has exactly the composition of starch.

By a boiling still longer continued, the dextrine is destroyed, and converted into starch-sugar, or grape-sugar. (See p. 920.)

When heated with moderately strong nitric acid, starch is converted into oxalic acid and other acids not exactly ascertained, but yields no mucic acid. Starch forms a soluble compound with potash, and insoluble compounds with oxide of lead, lime, and baryta.

When starch is bruised, by grinding it with some hard powder, the outer envelope of the grains is broken, and, if now placed in water, it swells up into a jelly. The same change takes place when starch is thrown into water at 140°. The envelopes burst, and a jelly is formed. But the starch is not dissolved; for, if the jelly be placed on bibulous paper, it shrinks up from the loss of water, and leaves a horny mass, insoluble in cold water, but easily soluble with the aid of heat. The outer coating is generally left undissolved, and amounts to 0·003 or 0·004 of the starch, but may be dissolved by long boiling. The gelatinous starch has been called Amidine, but its composition is the same as that of starch.

According to the recent experiments of Jaquelain, (Ann. de Ch. et de Phys. lxiii. 167,) when starch is heated in a digester with 5 to 15 parts of water, to 302°, everything is dissolved but the outer coats; and the solution, which is quite thin, deposits, on cooling, starch in minute granules, $\frac{1}{12700}$th of an inch in diameter. These are more soluble than the original starch, and are coloured blue by iodine. Their composition is the same as that of starch dried at 212°; but Jaquelain states that starch in all forms contains about 0·25 per cent. of nitrogen, which he considers essential. The formation of these granules indicates the presence of some organic property, and in common starch the structure shows this still more distinctly. This degree of organisation is one of the most important characters of starch.

With bromine starch forms an orange compound; with iodine, as already mentioned, a blue one. This latter, when pure, is not crystallised; and, although some consider it a definite compound, it is more probable that its colour is owing to finely divided iodine mechanically mixed with starch, or combined with it in the same way as a dye-stuff is united to the fibre of cloth.

Dextrine.—This substance is formed either by the action of diluted acids on starch at the boiling temperature continued for a certain time, or by the action of an infusion of malt on a solution of starch kept for some time at 150°. The addition of alcohol precipitates the dextrine. There appear to be two varieties; one coloured reddish purple by iodine, the other not coloured by that reagent.

Its name is derived from the action of its solution on polarised light, as it causes the plane of polarisation to deviate to the right. (Biot.) Its solution is not gelatinous, and it resembles gum. Its composition is the same as that of starch.

By the action of hot diluted acids, or of an infusion of malt, dextrine is finally converted into grape-sugar.

When dry starch is roasted, it is converted into a brownish transparent gum, soluble in cold water, and much used in calico printing. This is probably identical with dextrine.

Diastase.—This name has been given to the substance contained in malt which effects the conversion of starch into dextrine and grape-sugar. It is precipitated from a cold infusion of malt, by the addition of alcohol, as a white powder, soluble in water and tasteless. It contains nitrogen, and is probably analogous to gluten; but its composition, in a state of purity, is not known. It is said that 1 part of diastase will convert into sugar 2000 parts of starch. Its action probably depends on its undergoing spontaneous decomposition or putrefaction in contact with the starch, just as the conversion of sugar into alcohol and carbonic acid is caused by the putrefaction of gluten, &c. It is remarkable that its first effect seems to be to separate the external coat from the grains of starch.

The amount of diastase in malted barley is but small, not more than $\frac{1}{500}$th part. It is, however, by the action of this small proportion that the starch of the barley is converted into sugar, in the first stage of brewing, preparatory to the fermentation by which ale or malt spirits is obtained.

Inuline.—This variety of starch occurs in the root of *Inula Helenium*, in some lichens, and in the root of the Dahlia. It is very soluble in hot water; but, if moderately diluted, does not, like common starch, gelatinise on cooling. Its solution is not coloured blue by iodine; but, if so far concentrated as to deposit some of the starch on cooling, the addition of tincture of iodine to the hot solution yields a blue colour after cooling. (Liebig.)

The formula of inuline is $C_{24}H_{21}O_{21}$; and with oxide of lead it forms two compounds, $C_{24}H_{21}O_{21},5PbO$, and $C_{24}H_{18}O_{18},3PbO$. (Parnell.) As the formula of inuline in the latter compound is exactly twice that of starch, these results require confirmation.

Moss or *Lichen starch.*—This is found in *Cetraria Islandica* and other lichens. It forms a white opaque jelly. Its solution, if moderately diluted, is not coloured blue by iodine; but if it be concentrated so as to gelatinise on cooling, and tincture of iodine added to the hot liquid, the jelly is coloured blue. (Liebig.) This reaction is favourable to that view which considers the blue produced by iodine as not a compound, but starch dyed by iodine.

According to Guerin-Varry, the formula of this variety of starch is $C_{10}H_{11}O_{10}$.

Starch is one of the most important substances in the vegetable kingdom. Its ready convertibility, without change of composition, into soluble forms, such as dextrine and sugar, adapt it admirably for carrying on those changes which occur in the juices of vegetables. It is stored up in the seeds, roots, and pith of plants, and by its decomposition furnishes the materials for many of the most essential vegetable products. It also serves as a most important element of the food of animals, furnishing not indeed the means of increase of mass, but the materials for keeping up respiration and supplying the animal heat. The fats and fixed oils of the vegetable as well as the animal kingdom are in all probability derived principally from the deoxidation of starch.

Gum occurs in almost all vegetable juices, and frequently exudes in drops from the bark of trees, especially *Acacia* and *Prunus*. Formula, $C_{12}H_{11}O_{11}$.

Gum forms irregular, amorphous, transparent masses, sometimes nearly colourless, often yellow and brown. It is soluble in cold water, forming a mucilaginous solution, from which alcohol precipitates the gum. Subacetate of lead also causes a white precipitate. By the action of a heat of 266° gum loses 1 at. of water, but is changed in its properties. Strong nitric acid converts it into mucic acid.

Gum Tragacanth differs from ordinary gum in being insoluble in cold water, with which it swells up into a mucilaginous mass. With boiling water it forms a mucilage like that of ordinary gum.

Gum is much used in preparing water-colours, in calico-printing, and in medicine as a demulcent.

Woody fibre, or *Lignine*.—This name is given to the fibrous matter which forms the basis of wood, and of the stems and leaves of herbaceous plants. It is insoluble in all ordinary solvents, and is left after vegetables have been exposed to the successive action of ether, alcohol, water, diluted acids, and diluted alkalies.

According to Prout, the formula of lignine, when dried between 300° and 350°, is $C_{12}H_8O_8$. It forms about 95 per cent. of baked wood, and is the chief ingredient of linen, paper, and cotton. According to Payen, the tissue of wood is composed of $C_{12}H_{10}O_{10}$, and is isomeric with starch; while pure lignine fills the cells, and is $C_{35}H_{24}O_{20}$.

The composition of wood differs but little from that of lignine. Oak wood, according to Gay-Lussac and Thenard, is $C_{36}H_{22}O_{22}$. But wood contains mineral substances, which form its ashes when it is burned.

When lignine, in the form of straw, &c. is mixed with oil of vitriol, there is produced, besides dextrine or a substance resembling it, an acid, lignosulphuric acid, which forms soluble salts with baryta and oxide of lead. The dextrine, by boiling with the acid, is converted into grape-sugar. (See p. 921.) In strong nitric acid, saw-dust dissolves; and, on the addition of water, a white insoluble powder is deposited, which contains nitric acid, and explodes when heated. (Robiquet.)

When exposed to air and moisture, wood suffers decay or eremacausis, and is said to moulder, being gradually converted into a dark brown or black powder, called Mould, or sometimes Humus. The longer the decay has operated, the greater is the proportion of carbon in the residue. Thus oak wood is $C_{36}H_{22}O_{22}$; and one specimen of oak humus, analysed by Meyer, was found to contain $C_{35}H_{20}O_{20}$; and another, examined by Will, $C_{34}H_{18}O_{18}$: showing that, for every two equivalents of hydrogen oxidised by the air, one equivalent of carbonic acid had separated.

This decay of wood is prevented by antiseptics, and especially by corrosive sublimate, which seems to combine with the lignine. Were the decay to continue till all the hydrogen had been removed, wood, $C_{36}H_{22}O_{22}$, would leave only carbon, C_{25}; but this final result never occurs in nature under ordinary circumstances, because the excess of carbon holds the last portions of hydrogen with an increasing affinity as the amount of hydrogen diminishes.

It is probable, however, that the decay of lignine, in certain circumstances, may proceed to this extreme point; and if the carbon should be separated in a liquid, or in such a situation as to allow the particles to arrange themselves freely, it might crystallise, and thus yield the diamond. At all events, no other means are known by which diamonds can have been produced; and the recent discovery of the skeletons of organised tissues in the ashes of the diamond, which are the ashes of impurities enclosed in the crystals, has greatly added to the probability of this view of the origin of the diamond.

When wood is decomposed by the action of water in the absence of air, the process is properly termed Mouldering, to distinguish it from eremacausis or decay, in which oxygen is the active agent. In mouldering, oxygen is not, it is true, entirely excluded; but its access is limited, and the results are different. The elements of water, along with some oxygen, are taken up, and carbonic acid escapes. Thus, when oak wood was decomposed by lying under water, a white mouldered matter was formed, containing $C_{33}H_{27}O_{24}$. This is derived from oak wood, $C_{36}H_{22}O_{22}$, by the addition of $5HO + O_3$, and the subtraction of $3CO_2$. Mouldered beech yielded $C_{33}H_{25}O_{24}$, which may be accounted for in a similar way.

Wood coal, or *Brown coal*, has been produced by a similar action. A pure specimen of wood coal from Laubach contained $C_{33}H_{21}O_{16}$; that is, a greater proportion of carbon and hydrogen, and a smaller proportion of oxygen, than wood.

If wood were to lose 3 at. of carbonic acid and 1 at. of hydrogen, such a wood coal would be the result;

For if from wood, $=C_{36}H_{22}O_{22}$, we take
1 at. hydrogen, and 3 at. carbonic acid, $=C_3\ H\ \ O_6$, there
will be left wood coal $=C_{33}H_{21}O_{16}$.

Another specimen, from Ringkühl, contained $C_{32}H_{15}O_9$, and differs from wood by 4 at. carbonic acid, 5 at. water, and 2 at. hydrogen.

A specimen of wood, which had been long kept in the boiler of a steam-engine, acquired the appearance of wood coal, and had the same composition. In the formation of wood coal, the essential change seems to be the separation of carbonic acid from its elements, while a portion of hydrogen is removed by oxidation, owing to the limited access of air. The separation of carbonic acid seems still to go on even in the deepest beds of brown coal, and is the source of the acidulous springs found near such beds, and also of choke-damp in mines. When near the surface, the proportion of hydrogen in wood coal is always less, owing to the action of the air, by the oxygen of which the hydrogen is removed.

Mineral coal appears to be produced by a long-continued decomposition of wood or of wood coal, by which carbonic acid, water, and carburetted hydrogen are separated. Splint coal, and cannel coal, according to Richardson and Regnault, are both $C_{24}H_{13}O$, which may be thus derived from wood:

3 at. carburetted hydrogen	C_3H_6	$C_{36}H_{22}O_{22}$ = wood
3 at. water	H_3O_3	
9 at. carbonic acid	$C_9\ \ O_{18}$	$C_{12}H_9\ O_{21}$
Mineral coal		$C_{24}H_{13}O$

Caking coal is $C_{20}H_9O$, or cannel coal *minus* olefiant gas, C_4H_4. (Liebig).

This explains the occurrence of fire-damp, or carburetted hydrogen, in coal-mines; whereas, in mines of wood coal, carbonic acid, or choke-damp, alone occurs. The occurrence of fire-damp proves that changes are constantly occurring in the beds of coal. When the whole of the hydrogen is removed in the form of carburetted hydrogen, the residue must be anthracite, which is nearly pure carbon.

Besides carbonic acid and light carburetted hydrogen, fire-damp, according to Bischoff, contains olefiant gas and nitrogen; the latter probably derived from the atmospheric air, although most specimens of coal contain nitrogen originally derived from the juices of the wood.

Some varieties of coal contain oily and resinous matters; and in some cases an oil, like oil of turpentine, may be obtained by distilling the coal with water. (Reichenbach.) It is possible that these oils and naphtha may be formed out of the elements of the carbonic acid and carburetted hydrogen separated from the wood during its conversion into coal; but if the wood have been originally pines, then the resin and oil of turpentine may have been originally present in it.

On the whole, the production of wood coal and mineral coal may be considered, not as a case of eremacausis, but as a process to which oxygen is not essential, and in which the elements present group themselves into new arrangements, in a manner somewhat analogous to what occurs in fermentation.

The brown acids discovered by Berzelius in certain mineral waters, and called by him *Crenic* and *Apocrenic* acids, appear to be modifications of humus, and are no doubt derived from the decay of vegetable matter.

PRODUCTS OF THE ACTION OF HEAT ON WOOD AND COAL.

When wood is heated in close vessels, a variety of products are formed, some of which are solid, some liquid, and others gaseous. The gaseous products are chiefly carburetted hydrogen.

The liquid products separate into two portions, of which one is watery and acid, the other composed of tar and oily liquids. The watery portion contains much water and acetic or pyroligneous acid, pyroxylic spirit or hydrated oxide of methule (see pp. 877 and 953), and a good deal of the oily matters dissolved. The tar and oil contain a variety of new compounds, all combustible, and composed either of carbon and hydrogen, or of carbon, hydrogen, and a little oxygen.

The solid products are, charcoal left in the retort, and certain crystalline volatile compounds, which are found dissolved in the oil of tar. Of these, paraffine and naphthaline are carbohydrogens, while pyroxanthine contains also oxygen.

Having already described the gaseous carbohydrogens, pyroligneous acid, and pyroxylic spirit, we shall now give a brief account of the remaining products found in wood tar.

Eupion.—Discovered by Reichenbach. It is said by some to have the formula C_5H_6; by others, to be isomeric with olefiant gas. It may be obtained by repeated rectifications of oil of tar; but, as strong acids and alkalies were used in its purification, there is some reason to think, that, as finally obtained, it is a product of the decomposition of some other oil.

It is a very limpid, mobile, colourless fluid, of sp. g. 0·655, which has a fragrant odour, and burns with a clear luminous flame. According to Reichenbach, it boils at a very low temperature, not above 100° F.; but in the experiments of others so volatile a liquid has not occurred. It is not altered by potassium, iodine, acids, or alkalies.

It appears that no other chemist has succeeded in obtaining eupion with precisely the characters ascribed to it by Reichenbach, and each experimenter has obtained a different modification of it. All these liquids, however, have a similar composition, which is either isomeric with olefiant gas, or very nearly so.

Creosote.—Formula, $C_{14}H_9O_2$. (Ettling.) This is the antiseptic principle of wood smoke, pyroligneous acid, and tar; and gives the smoked flavour to meat cured by smoke or pyroligneous acid. It is purified by repeated distillations, and by combination with potash, the process being very tedious. (Reichenbach.) It is an oily, colourless, highly refracting liquid, of sp. g. 1·037, boiling at 397·4°, and burning with a smoky flame. It has a burning taste, and a strong smell of wood smoke, or rather of peat smoke. It combines with 80 parts of water, and is very soluble in acetic acid and alcohol. It also combines with potash, forming an oily anhydrous compound, and a hydrated one which crystallises.

Creosote possesses remarkable antiseptic properties; meat steeped in its aqueous solution may be preserved for a long period, and acquires a delicate smoked flavour, if the creosote be pure. This property appears to depend upon its action on albumen, which it instantly coagulates, and renders unsusceptible of putrefaction. Its name is derived from κρεας, flesh, and σωζω, I preserve. It dissolves a large number of organic substances, especially resins, gum-resins, and colouring matters.

As a remedy, creosote is very valuable. In the pure state, in that of ointment, or in the aqueous solution, it may be applied with the most decided benefit to almost all ulcers, wounds, and cutaneous affections. It promotes healing, and is very manageable. Internally it has been found very beneficial in cases of obstinate vomiting; but the dose must be carefully regulated, as it is poisonous in a certain quantity. One or two drops in a cup of water may be safely tried. Its solution is a very valuable styptic, and checks bleeding from wounds and cuts, probably by coagulating the blood, and thus closing the wounded vessel. In cases of toothache arising from a decayed tooth, the application of pure creosote to the hollow, so as to touch the diseased nerve, is seldom known to fail in instantly removing the pain, and is often followed by a long exemption from suffering. Care must be taken not to swallow it, nor even to allow it to escape into the mouth, as it produces excoriation in the latter case. In toothache it probably acts by coagulating the secretions, and thus protecting the nerve from the atmosphere; but it certainly diminishes inflammation in ulcers when applied to them. The inhalation of its vapour has been recommended in consumption with ulceration of the lungs, and it will probably afford relief.

For the introduction of this valuable remedy we are indebted to Dr. Reichenbach, its discoverer. It may be added, that the editor has applied it successfully to external and cutaneous affections in horses and dogs; and that it is a valuable application to sheep, as it destroys the insects that infest them, without soiling the wool, as tar does, when used for the same purpose.

Picamar (in pice amarum) is a bitter oil, also discovered in tar by Reichenbach. Its sp. g. is 1·10, and it boils at 518°. It forms crystalline compounds with alkalies, but does not neutralise them. It requires further investigation.

Capnomor (from καπνος, smoke, and μοιϱα, a part) is another oily fluid, discovered in tar by Reichenbach. It is little known.

Pittacal (from πιττα, pitch, and καλος, beautiful) is a solid of a fine indigo-blue colour, assuming, when its surface is polished, the lustre of gold, which was obtained by Reichenbach from the action of baryta on a certain portion of the oil of tar. It is probably a product of the decomposition of some other substance by the baryta. It is coloured red by acids, and the colour restored by alkalies. It is insoluble in water, but may be suspended so as to pass through a filter. It would probably be available as a dye, if it could be procured easily; but Reichenbach has not yet published the process by which it is obtained. It is certain that baryta-water developes a blue colour in some specimens of oil of tar.

Cedriret is another solid compound, also discovered by Reichenbach in tar. It forms a network of red crystals, but has hardly been studied.

Paraffine (from parum and affinis, because it is a highly indifferent compound). Discovered in tar by Reichenbach. It is also found in the products of the distillation of wax (Ettling), and in the petroleum of Rangoon (Christison; Gregory). Formula, CH, or some multiple of this.

It is a white fusible solid, resembling wax, and may be obtained from its solution in hot ether in shining scales. It may be distilled unchanged. Sp. g. 0·870. It burns with a clear white flame, like wax. It is not acted on by chlorine, alkalies, or acids.

Naphthaline.—According to Reichenbach, naphthaline occurs among the products of the distillation of wood; but, as it is more characteristic of coal tar, we shall describe it as a product of the distillation of coal.

When coal is distilled, it yields, besides coke, coal gas, a mixture of light carburetted hydrogen, olefiant gas, and the vapours of several volatile carbohydrogens; also, a watery liquid containing ammonia and hydrocyanic acid; and, finally, tar and oil, containing most of the ingredients of wood tar, with a large proportion of napththaline.

Runge has described, under the names of carbolic acid, rosolic acid, brunolic acid, leucole, pyrrole, and cyanol, a number of compounds derived from coal tar, some of which are obviously mixtures of creosote with other oils. Liebig is of opinion, that the carbolic acid of Runge is the same as the hydrate of phenyle of Laurent; but the whole of these compounds require renewed investigation.

Naphthaline.—Formula, $C_{20}H_8$. It crystallises from the oil of coal tar after it has been rectified, and is purified by crystallisation from alcohol. It forms shining plates, of a strong and peculiar odour, volatile, fusible at 176°, boiling at 423°. It burns with a smoky flame.

When acted on by anhydrous sulphuric acid, it forms several acids, of which the best known is sulphonaphthalic or hyposulphonaphthalic acid, $C_{20}H_8S_2O_5,HO$. It forms a soluble salt with baryta, neutralising just as much base as the hyposulphuric acid which it is supposed to contain.

When dissolved in excess by sulphuric acid, and precipitated by water, naphthaline is partially altered, yielding two new compounds, not volatile, as naphthaline is, with the vapours of water; namely, sulphonaphthaline, $C_{20}H_8SO_2$, and sulphonaphthalide, $C_{24}H_{10}SO_2$. Both are insoluble in water.

The action of chlorine on naphthaline is peculiar, and has been studied by Laurent. When naphthaline is exposed to chlorine gas at the ordinary temperature, it absorbs the gas and yields a yellow oil, $C_{20}H_8Cl_2$, or $C_{20}H_7Cl,HCl$. When this compound, which is called the hydrochlorate of chloronaphthalase, is treated with potash, it loses HCl, leaving chloronaphthalase, $C_{20}H_7Cl$.

When chlorine acts on naphthaline at 140°, there is produced the hydrochlorate of chloronaphthalese, $C_{20}H_8Cl_4$, or $C_{20}H_6Cl_2,2HCl$. This is solid, fusible, and crystallises from ether in rhomboidal tables. When acted on by an alcoholic solution of potash, it yields chloronaphthalese, $C_{20}H_6Cl_2$, losing 2HCl. Chloronaphthalese crystallises from alcohol in rhombic prisms, and melts at about 111°.

When chlorine is made to act in the sunshine on the fluid compound first described, there is obtained another crystallisable compound, *chloronaphthalise*, $C_{20}H_5Cl_3$. It is fusible at 163°.

By the action of chlorine on chloronaphthalese, $C_{20}H_6Cl_2$, at the ordinary temperature, there is formed the *hydrochlorate of chloronaphthalose*, $C_{20}H_4Cl_4,2HCl$. It fuses at 105·8°, and may be sublimed unaltered.

In the substances above described, which were discovered by Laurent, the hydrogen of naphthaline is gradually replaced by chlorine, while some of the compounds produced unite with hydrochloric acid. The replacement of 1, 2, or 3 atoms of hydrogen, &c. is indicated by the use of the vowels, *a*, *e*, *i*, *o*, in the names.

When naphthaline is heated with nitric acid, 1 at. of water separates, and there is formed *nitronaphthalase*, $C_{20}H_7 + NO_4$. It forms yellow prisms, fusible at 109·4° and volatile. If the action of nitric acid be longer continued, there is obtained, in the form of a yellow crystalline powder, *nitronaphthalese*, $C_{20}H_6 + 2NO_4$, in the formation of which 2 atoms of water have been separated.

By the action of nitric acid on the chlorinised compounds of naphthaline, Laurent has obtained the following new compounds. 1. *Oxichloronaphthalose*, $C_{20}H_4Cl_2O_2 + HO$. 2. *Chloronaphthalosic acid*, $C_{20}H_4ClO_3 + O_2$. 3. *Naphthalosic acid*, one-half ($C_{16}H_4O_4 + O_2$;) and 4. *Oxichloronaphthalenose*, $C_{18}H_4Cl_3O$.

De Marignac obtained, by continuing still further the action of nitric acid on naphthaline, another body, *nitronaphthalise*, $C_{20}H_{10}$

$+3NO_4$. By the action of alkalies it yields a *brown matter*, $C_{12}H_3NO_5$; and *nitronaphthalic acid*, $C_{16}H_5NO_{12},2HO$, which is bibasic and forms crystallisable salts.

The same chemist also discovered a volatile liquid, which distils over when the hydrochlorate of chloronaphthalese, $C_{20}H_8Cl_4$, is heated with nitric acid. Its composition is $CClNO_4$. It has not been named.

In this experiment an acid is formed identical with the *naphthalic acid* obtained in the same way by Laurent, which both chemists have found to be $C_8H_2O_3,HO$. This acid is crystallisable, fusible at 221°, and may be sublimed. It appears, however, from the most recent experiments of De Marignac and Laurent, to be a bibasic acid, $C_{16}H_4O_6,2HO$. With ammonia it forms an acid salt, $C_{16}H_4O_6,NH_4O,HO$. The acid, when sublimed, yields *anhydrous naphthalic acid*, $C_{16}H_4O_6$; and this last, when dissolved in ammonia, yields *naphthalamide*, $C_{16}H_4O_5,NH_2$. Naphthalamide, when heated to 250°, loses water and leaves *naphthalimide*, $C_{16}H_4O_4,NH$. Laurent has given to the naphthalic acid the name of Phthalic acid, as he considers it no longer to belong to the series of naphthaline.

The whole subject of the products derived from naphthaline, of which a very brief and imperfect account has been given above, requires further investigation. The composition of several of the compounds must be considered as yet doubtful, as in some cases one analysis only is given, and that is frequently deficient in regard to some of the elements.

Paranaphthaline: Syn. *Anthracene.* Formula, $C_{30}H_{12}$.—Accompanies naphthaline in coal tar, is isomeric with it, but is distinguished by its sparing solubility in hot alcohol. It fuses at 356°, and boils at 572° or higher. The density of its vapour is greater than that of the vapour of naphthaline in the proportion of 3 to 2. According to Laurent, it yields, like naphthaline, a numerous series of compounds when acted on by nitric acid and by chlorine.

Coal naphtha.—This is obtained by the rectification of coal tar. It is no doubt a mixture, and is important chiefly because it is the principal ingredient in the solvent for caoutchouc used in making waterproof cloth.

Petroleum and *Bitumen.*—Under these names are known certain natural tarry matters, more or less fluid, which have evidently resulted from the decomposition of wood or coal, either by heat, or by spontaneous action under the surface of the earth. The most celebrated are those of Persia and the Birman empire, and of Amiano in Italy. They contain paraffine, along with several liquids, all combustible and all composed of carbon and hydrogen. According to Pelletier and Walter, native napthha is composed of three liquids, namely *naphtha*, $C_{14}H_{13}$; naphthene, $C_{16}H_{16}$; and naphthole, $C_{24}H_{22}$. All these compounds have very similar properties.

There are other forms of bitumen, which are dark-coloured or black, and chiefly composed of solid matter, such as asphaltum and maltha. Their chemical history is little known.

Laurent has given the names of Pyrene and Chrysene to certain carbohydrogens obtained from coal tar, and that of Phene to benzole or benzine, $C_{12}H_6$. (See p. 793.) He considers the hydrate of phene (hydrate of phenyle) to exist in coal tar, and to be $C_{12}H_8O_2 = C_{12}H_6,2HO$. From this he deduces the composition of a number of compounds formed by the action of chlorine, &c. on the liquid parts of coal tar. It is impossible in this work to do more than allude to the very voluminous and detailed researches of Laurent, as well on naphthaline, as on anthracene and the substances just mentioned. Many of his results require confirmation, and the details will be found in the original memoirs in the Annales de Chimie et de Physique.

INDIFFERENT AZOTISED SUBSTANCES, COMMON TO THE VEGETABLE AND ANIMAL KINGDOMS.—PROTEINE AND ITS MODIFICATIONS.

Under this head we have to consider a few very important compounds, which are formed in the vegetable kingdom, and are also found to constitute a large proportion of the animal body. These are *Albumen*, *Fibrine*, and *Caseine*. Till very recently, it was believed that vegetable albumen and fibrine differed from animal albumen, fibrine, and caseine; but the recent researches of Mulder have shown that this opinion was erroneous, and Liebig has demonstrated that caseine exists in vegetables with all the characters of that found in milk.

The most important step recently made in advance in this important investigation is doubtless the discovery, made by Mulder, that albumen, fibrine, and caseine are all nothing more than modifications of one compound, to which he has given the name of Proteine, (from πρωτευω, I take the first place,) as being the original matter from which all these varieties are derived.

Proteine is composed of carbon, hydrogen, nitrogen, and oxygen; and Mulder has shown, that two analyses of proteine do not differ more than analyses of fibrine, albumen, or caseine do, either from one another or from that of proteine, as far as regards these elements. He has further shown that all of these bodies, whether they contain proteine ready formed or not, readily yield it when acted on by alkalies. While proteine, however, contains no inorganic matter, albumen, fibrine, and caseine each contain small but essential quantities of mineral substances, such as sulphur, phosphorus, potash, soda, common salt, and phosphate of lime. Further, it has been established by the still more recent researches of the school of Giessen, that animal and vegetable albumen, animal and vegetable fibrine, and animal and vegetable caseine are respectively identical in every particular. We may therefore assume that there is but one albumen, one fibrine, and one caseine; and it is convenient to consider them all as compounds of proteine with small proportions of inorganic matter.

Proteine. — When animal or vegetable albumen, fibrine, or caseine are dissolved in a moderately strong solution of caustic potash, and the solution heated for some time to 120°, the addition of acetic acid causes the formation of a gelatinous precipitate, which has the same composition and properties, from whichever of these compounds it has been prepared. When well washed and dried, this is proteine.

It forms a yellowish brittle mass, insoluble in water and alcohol. Mulder has analysed proteine from animal and vegetable albumen, from fibrine and from cheese, or caseine; and Scherer has analysed proteine from animal albumen and fibrine, from the crystalline lens, from hair, and from horn. The results from all these analyses agree best with the formula $C_{48}H_{36}N_6O_{14}$ (Liebig); Mulder first gave the formula, $C_{40}H_{31}N_5O_{12}$. Its symbol is Pr.

Proteine combines with both acids and bases: with diluted sulphuric acid it forms sulphoproteic acid, $Pr + SO_3$; with diluted hydrochloric acid, another acid, $Pr + 2HCl$. When chlorine is passed through a solution containing proteine, white flocks are deposited, which Mulder calls Chloroproteic acid, $Pr + ClO_3$. (Mulder.)

When proteine, or any of its modifications, is digested in nitric acid, a yellow compound is formed, along with oxalic acid and ammonia. The yellow compound is called Xanthoproteic acid, and its formula is $C_{34}H_{24}N_4O_{12}, 2HO$. It seems to combine both with acids and bases. Its salts with bases dissolve with a red colour. (Mulder.)

When boiled with an excess of caustic potash, proteine, albumen, &c. are decomposed, yielding, besides ammonia and carbonic and formic acids, three azotised products, protide, erythroprotide, and leucine. Erythroprotide is a reddish brown amorphous mass; and its formula, in the compound it forms with oxide of lead, is said to be $C_{13}H_8NO_5$. Protide is a yellowish, soluble, uncrystallisable substance, and its formula is $C_{13}H_9NO_4$. Leucine crystallises in shining scales, which sublime unaltered at 338°. Its formula is $C_{12}H_{12}NO_4$. With 1 atom of hydrated nitric acid it yields nitroleucic acid, which forms crystallisable salts. Leucine may also be formed by the action of sulphuric acid on proteine or its compounds. (Mulder.)

According to Mulder, proteine combines with the oxides of lead and silver in the proportion of ten atoms to one of the base: and the same amount of proteine is contained in albumen and fibrine; the former being $10Pr + S_2 + P_{\frac{1}{2}}$, the latter $10Pr + S_4 + P_{\frac{1}{2}}$.

According to Liebig, (Animal Chemistry, p. 106,) proteine is produced by vegetables alone, and cannot be formed by animals; although the animal organism possesses the power of converting one modification of proteine into another, fibrine into albumen, or *vice versâ*, or both into caseine, &c. In this point of view the vegetable forms of proteine, vegetable albumen, fibrine, and caseine, become signally important, as the only sources of proteine for animal life, and consequently of nutrition strictly so called, that is, the growth in mass of the animal body.

Proteine is never found, as such, in nature; but occurs in the shape of albumen, fibrine, or caseine, both in vegetables and animals, and in some other forms in the animal body.

MODIFICATIONS OF PROTEINE.

Albumen.—This important substance forms the white of eggs, and occurs in large quantity in the blood. It is also found in other animal fluids, and in most of the animal solids.

It occurs also in many vegetable juices, and in many seeds, such as nuts, almonds, &c. From whatever source it is obtained, its properties are the same.

Albumen is naturally soluble in water, and is found dissolved in the serum of the blood, and in vegetable juices. The white of eggs is quite soluble; and the albumen of wheat-flour also dissolves in water, if it have been purified without the application of heat. But, when it has once been heated to 160°, it becomes insoluble; and, if previously dissolved, a heat of 158° causes the dissolved albumen to coagulate, and the coagulum is insoluble in water. Hence albumen is described in two states, the soluble, and the coagulated.

If white of egg, or serum of blood, be dried up at 120°, the residue is soluble albumen in an impure state; it is purified by being well washed with cold ether and alcohol, which remove fat, salts, and other foreign matters.

Dry soluble albumen, when placed in water, first swells up, and then forms a glairy fluid. This solution is coagulated by heat, by acids, by alcohol, by creosote, &c. The acids which do not coagulate albumen are acetic acid, phosphoric and pyrophosphoric acids. The coagulated albumen dissolves with the aid of heat in strong hydrochloric acid, producing a purple solution. This reaction applies to all the modifications of proteine, and indicates a great similarity of constitution among them.

The solution of albumen is also coagulated or precipitated by the ferrocyanide of potassium if acetic acid be added; by the acetate of lead, and the bichloride of mercury; also by infusion of galls. From the insolubility of the precipitate with bichloride of mercury, white of egg, beat up with water, is used as an antidote to that poison. One egg combines with about four grains of corrosive sublimate.

The precipitates formed by acids are compounds of albumen with the acid employed. They are soluble in pure water, but quite insoluble in diluted acids.

Coagulated albumen is quite insoluble in water, but is readily dissolved by caustic alkalies, which it even neutralises. These compounds yield insoluble albuminates with the metallic salts.

Coagulated albumen, when acted on by hydrochloric acid, yields from 1 to 2 per cent. of phosphate of lime; and soluble albumen appears to possess the property of dissolving that salt, a property which enables the blood to convey to the bones their earthy part, and probably also to carry away that which is found in the urine.

When albumen is analysed, it yields the same results as proteine, in regard to carbon, hydrogen, nitrogen, and oxygen; but it contains less than 1 per cent. of sulphur and phosphorus together, which are absent in proteine. According to Mulder, it is $10Pr + S_2 + P\frac{1}{2}$; but we have no means of determining with accuracy such small proportions of sulphur and phosphorus, and it is therefore preferable to represent albumen as proteine with certain small indeterminate proportions of sulphur and phosphorus. When burned, it also leaves ashes, which contain phosphate of lime and alkaline salts.

To prove the presence of unoxidised sulphur in albumen, dissolve it in potash, then add acetate of lead as long as the precipitate formed is redissolved, and heat the solution to the boiling point. It instantly becomes black by the separation of sulphuret of lead. The same test applies to fibrine and caseine. (Liebig.) It is not known in what state the phosphorus exists in albumen, after phosphate of lime has been separated. The fetid smell of putrefying albumen indicates distinctly the presence of sulphuretted hydrogen among the products of its putrefaction.

When the juice of many vegetables, after being separated from the coagulum or deposit, which spontaneously forms in it, and which is vegetable fibrine, is heated, a new coagulum is formed, which is vegetable albumen. When nuts, almonds, and similar seeds are freed from their oil by pressure, the residue is chiefly vegetable albumen in the soluble form. It is in every respect identical with the albumen of eggs and of blood.

Albumen must be considered as the true starting point of all the animal tissues. This appears from the phenomena of incubation, where all the tissues are derived from the albumen of the white and of the yolk, which contains albumen also, with the aid only of the air, of the oily matter of the yolk, and of a certain proportion of iron, also found in the yolk. It is clear from this, that albumen may pass into fibrine, caseine, membranes, horn, hair, feathers, &c.

Fibrine.—This modification of proteine occurs, like albumen, in two forms, dissolved and coagulated. The former is found in fresh-drawn blood and in fresh-drawn vegetable juices, from both of which it coagulates spontaneously on standing. In the coagulated state it is found in muscular fibre, and in the gluten of wheat-flour and the seeds of the cerealia generally.

The characters of insoluble or coagulated fibrine closely resemble those of coagulated albumen. With strong acetic acid it forms a jelly, which may be dissolved by boiling water, and is precipitated by ferrocyanide of potassium. It is similarly acted on by other acids; and, like albumen, dissolves in alkalies, which it neutralises. It gives a purple solution with strong hydrochloric acid.

When fresh blood is allowed to stand, the fibrine dissolved in it coagulates very soon, and forms the clot, which, however, is coloured by the globules of the blood; but, if the blood be stirred with a stick while coagulating, the fibrine adheres to the stick in grey stringy masses, which dry, like albumen, into a horny matter. Like albumen, it contains sulphur and phosphorus, and its ashes contain phosphate of lime. It contains less sulphur, however, than albumen.

As albumen, during incubation, passes into fibrine, so fibrine in the animal body passes into albumen; for example, in the case of an animal fed on muscular fibre, whose blood contains the usual proportion of albumen. Nay, Denis has shown that the fibrine of venous blood, by digestion with a solution of nitre, is dissolved, and acquires the characters of albumen, being coagulated by heat and by acids. Scherer has shown that the fibrine of arterial blood does not undergo this change, nor that of the buffy coat, nor even venous fibrine after exposure to the air for some time. Hence he concludes that it is rendered incapable of dissolving by the action of oxygen, and that the fibrine of venous and of arterial blood are thus distinct; the former being soluble, the latter coagulated.

He found that the above-mentioned solution of venous fibrine in nitre, when exposed to the air, deposited an insoluble matter, identical with arterial fibrine. He also observed, that, after being boiled for a short time, venous fibrine became insoluble, and had lost the property, possessed by it when fresh, of absorbing oxygen and giving off carbonic acid.

The fibrine which spontaneously coagulates from certain vegetable juices, such as those of carrots, turnips, and beet-root, and that contained in the gluten of wheat-flour, are identical in properties and composition with animal fibrine.

Fibrine, both animal and vegetable, is a most important element of nutrition; and yields, in the animal body, albumen, caseine, and the tissues derived from them.

Caseine.—This, the third important modification of proteine, is found in milk, and constitutes that ingredient which is neither coagulated spontaneously, like fibrine; nor by heat, like albumen; but by the action of acids alone. Cheese, made from skimmed milk and well pressed, is nearly pure caseine. A substance quite identical is found abundantly in the seeds of leguminous plants, and was formerly called *Legumine.* Liebig has recently shown that legumine is nothing but caseine; and, from whatever source, it is found to be a compound of proteine. Thus its analysis gives the same results as those of fibrine and albumen for the four organic elements; and it differs from these bodies in containing no free phosphorus. Its ashes are very rich in phosphate of lime and in potash; and in this point also animal and vegetable caseine agree.

Coagulated caseine is generally a compound of caseine with the acid employed to coagulate it. When milk, on standing long, coagulates, it is found to contain free lactic acid, some of which by combining with the caseine has caused the precipitate. When sulphuric acid is used, the coagulum is sulphate of caseine; which, when the acid is removed by carbonate of lead, yields pure caseine.

When dry, caseine thus prepared is like gum. It is not readily dissolved by water, and never forms a clear solution. It is precipitated by acetic acid, but in other respects resembles a solution of albumen, except that it is not coagulated by heat. When milk is placed in contact with *rennet,* which is the lining membrane of a calf's stomach, it is coagulated. Liebig has shown, that, unless the membrane be in a state of decomposition, this change does not take place; and it probably depends on the formation, under the fermenting influence of the membrane, of sufficient lactic acid to neutralise the alkali of the milk and thus coagulate the caseine. When sweet milk or cream is used, the cheese contains much butter besides the caseine.

When milk is heated in an open vessel, a pellicle is formed, which, if removed, is continually renewed, and is insoluble. It is owing to the action of oxygen, for it does not form in an atmosphere of carbonic acid. (Scherer.)

When peas, beans, or lentils are softened in cold water, then ground with that fluid, and the mass further diluted, and strained through a fine sieve, there passes through a solution of caseine in which starch is suspended. When the starch has settled, the supernatant liquid is a solution of caseine, which is always, like milk, turbid, partly from suspended fat, partly from the gradual action of the air on the dissolved caseine, lactic acid being slowly formed, which causes a gradual separation.

This solution has all the characters of skimmed milk; it is coagulated by acids, not by heat, and forms a pellicle when heated. It also coagulates after long standing from the formation of lactic acid; and, when the coagulum putrefies, the odour is exactly that of putrid cheese. (Liebig.)

The ashes of soluble caseine, whether animal or vegetable, are very strongly alkaline; and there is reason to believe that the potash found in the ashes had served, by combining with the caseine, to render it soluble.

Caseine occurs also in the oily seeds, such as almonds, nuts, &c., along with albumen, and must be considered as a very important element of nutrition.

Scherer, by acting on the serum of blood with water and a little caustic potash, obtained a neutral solution, which no longer coagulated by heat, but formed a pellicle like milk. As this pellicle appeared identical with that from milk, the experiment seems to prove the conversion of albumen into caseine.

Mulder considers caseine to be $10Pr + S$; but pure caseine is not known, and caseine, as it usually occurs, contains 6·5 per cent. of inorganic matter, chiefly phosphate of lime and potash. There is no doubt, however, that the organic elements of caseine are united in the same proportion as those of proteine, albumen, and fibrine; while, like the two latter, it yields a purple solution when heated with strong hydrochloric acid. The action of milk, also, in the nutrition of young animals proves that caseine is capable of conversion into albumen and fibrine; while the production of milk in an animal fed on albumen or fibrine, or both, shows that these bodies may be reconverted into caseine.

We may exhibit the connection between these substances as follows. Pr represents proteine, $C_{48}H_{36}N_6O_{14}$. P and S. represent, not equivalents, but only small indeterminate quantities, of phosphorus and sulphur.

Albumen is .	$Pr+S_2+P+$ salts.
Fibrine is .	$Pr+S+P+$ salts.
Caseine is .	$Pr+S+$ salts.

We can thus easily understand the formation of any one of them from proteine, or the conversion of one into the other. Albumen, losing half its sulphur, becomes fibrine; and fibrine, losing its phosphorus, becomes caseine: but the salts are not exactly the same, nor in the same proportions in all the three cases.

THE BLOOD.

This important fluid, from which all parts of the body are formed, possesses very remarkable properties. In the veins it is dark-coloured, in the arteries bright red. When drawn, it presently forms a red clot, composed, as we have seen, partly of fibrine, while the serum contains a large quantity of albumen.

The colour of the clot is owing to a compound which has been called *Hæmatosine*, which has many properties in common with albumen; but the globules of the blood, in which the colour naturally resides, are not composed of hæmatosine alone, but contain another albuminous compound, to which the name of *Globuline* has been given. It is probable that neither of these compounds is known in a state of purity.

To obtain them, blood is well stirred to separate the fibrine, and mixed with 6 volumes of a saturated solution of sulphate of soda, in which the globules are insoluble. They are then boiled with alcohol acidulated with sulphuric acid, which dissolves a sulphate of hæmatosine, and leaves a sulphate of globuline. The red alcoholic solution is mixed with carbonate of ammonia, which separates the sulphuric acid as sulphate of ammonia, along with a little globuline. The filtered solution, being evaporated, leaves hæmatosine as a dark brownish red mass.

Hæmatosine thus prepared is insoluble in water, alcohol, and ether, but forms red solutions with alcohol, to which either acids or alkalies are added. Its ashes contain iron, but Liebig and Scherer have shown that the red colour does not depend on that metal, which may be removed either from the globules, or from hæmatosine, by strong sulphuric acid, without destroying the red colour; and in this experiment the red matter left gives a white ash, free from iron. Iron, however, is essential to the blood, and is consequently supplied in the food. The ashes of almost all vegetables contain a little iron; flesh of course does so, as it is mixed with blood; and the yolk of egg is found to contain an oily matter, of which iron is an ingredient.

Globuline forms the principal part of the blood-globules. It has not been obtained in a pure state, but has all the characters, as well as the composition, of dissolved albumen. The compound with sulphuric acid above mentioned is grey, or white, and was found to contain 4 atoms of sulphuric acid and 1 of proteine.

Besides albumen, the serum of the blood contains fat and saline matters. When heated, the albumen coagulates, and floats in a watery liquid called the *Serosity*. This contains common salt, sulphates, phosphates, and carbonates. The blood probably also contains the ingredients of the secretions and excretions, such as bile and urine; but these are in so small a proportion, that, except in cases of disease, it is hardly possible to detect them. The fatty matter in blood is obtained by drying up the serum and digesting with ether. It consists of the usual animal fats, and is said likewise to contain cholesterine, or the fat of bile.

The following table gives the results of two careful analyses of blood by Lecanu:

	Human blood.	
Water	780·145	785·590
Fibrine	2·100	3·565
Colouring matter (hæmatosine and globuline)	133·000	119·626
Albumen	65·090	69·415
Crystalline fat	2·430	4·300
Oily matter	1·310	2·270
Extractive matter (soluble in water and alcohol)	1·790	1·920
Albuminate of soda	1·265	2·010
Alkaline chlorides, carbonates, phosphates, and sulphates	8·370	7·304
Carbonates of lime and magnesia, phosphates of lime, magnesia, and iron, peroxide of iron	2·100	1·414
Loss	2·400	2·586
	1000·000	1000·000

It is obvious, that, as the blood is chiefly composed of compounds of proteine, its composition cannot be very different from that of proteine or its modifications. In fact, dried blood, when analysed, yields the formula $C_{48}H_{39}N_6O_{15}$, which is proteine, $C_{48}H_{36}N_6O_{14} + HO + H_2$. (Playfair and Boeckmann.) This excess of hydrogen is probably derived from the presence of fat.

From the blood, that is, from the compounds of proteine in the blood, are derived all the animal tissues. Some of these are compounds of proteine, others have no longer the characters of such compounds; but in all cases they are derived from proteine.

Muscular tissue, or *Muscular fibre*, is composed chiefly of fibrine, mixed however in the ordinary state with blood, membranes, nervous matter, and fat. Dried flesh, when analysed, gave the same formula as dried blood, namely $C_{48}H_{39}N_6O_{15}$. (Playfair and Boeckmann.)

When flesh is acted on by hot water, there is dissolved a quantity equal to 17 per cent. of its weight. The dissolved matter contains the salts of flesh, and several organic matters probably produced in the operation, the nature of which is very little known. One of these has been described under the name of Osmazome, and is supposed to give to soup and dressed meat their peculiar flavour: but osmazome is certainly not a pure substance, as at present known; and the whole subject of the changes produced in food by cooking is understood to be under investigation by Liebig.

Gelatinous tissue.—Under this name are included the organic tissue of the bones, that of tendons and ligaments, the cellular tissue, the skin, and the serous membranes. All these substances dissolve by long-continued boiling in water, and the solution on cooling forms a jelly. The coarser forms of gelatine, from hoofs, hides, &c. are called *Glue;* that from skin and finer membranes is known as *Size;* and the purest gelatine, from the air-bladders and other membranes of fish, is called *Isinglass.* Gelatine does not exist as such in the animal tissues, but is formed by the action of boiling water.

Gelatine is soluble in water, and the hot concentrated solution forms a jelly on cooling. It is precipitated by tannic acid, forming an insoluble compound, which forms the chief part of leather. Leather is made by steeping softened skins in a strong infusion of oak-bark, catechu, or other astringent vegetables containing tannic acid. Skins are prepared in other ways, yielding different kinds of leather, such as tawed leather, wash-leather, &c.; but the process of tanning depends on the action of tannic acid on the gelatinous tissue.

Gelatine, when acted on by sulphuric acid, yields *gelatine sugar* or *glycicoll*, $C_8H_7N_2O_5,2HO$. When treated with potash, it is said to yield glycicoll and leucine. Glycicoll unites with oxide of lead, forming a compound, $C_8H_7N_2O_5,2PbO$. (Mulder.) It also combines with nitric acid, forming a compound acid, $C_8H_7N_2O_5 + 2NO_5 + 4HO$, which crystallises, and forms double salts with bases. That with lime is $CaO,C_8H_7N_2O_5 + 2(CaO,NO_5)$.

According to Scherer, the composition of gelatinous tissue is represented by the formula $C_{48}H_{41}N_{7\frac{1}{2}}O_{18}$, or doubled, $C_{96}H_{82}N_{15}O_{36}$; which latter formula represents 2 at. proteine + $3NH_3$ + HO + O_7.

Although gelatine is thus nearly related to proteine, and is doubtless formed from one or other of its modifications, yet it has none of the characters of a compound of proteine. It does not yield proteine when acted on by potash, and it does not produce a purple colour with hydrochloric acid. It therefore no longer contains proteine.

This accounts for the fact, that animals, fed exclusively on gelatine, die with the symptoms of starvation. The gelatine, containing no proteine, cannot yield albumen, fibrine, or caseine; and it has already been stated that the animal system, although it can convert one form of proteine into another, cannot form proteine from compounds which do not contain it. Blood therefore cannot be made from gelatine, and the animal soon dies. But when mixed with other food, especially compounds of proteine, gelatine may be useful, and may serve directly to nourish the gelatinous tissues. (Liebig, Animal Chemistry, 98. 130.) This would explain the use of gelatine as a part of the food of convalescents, whose debilitated system cannot readily convert albumen, &c. into gelatine for the nutrition of these tissues, and finds it ready-made in the food. The experiments of D'Arcet on the gelatine from bones have proved, that, as part of the diet in hospitals, gelatine produces the best effects, and materially abridges the period of convalescence. When it is given alone, all animals soon refuse it with disgust, and die if confined to gelatinous food.

Chondrine.—This substance forms the tissue of cartilage as it occurs in the ribs, trachea, nose, &c. and of the cornea. It is slowly dissolved by boiling with water, and when dry resembles glue. But it differs from gelatine in not being precipitated by tannic acid, and in giving precipitates with acetic acid, alum, green vitriol, and acetate of lead. Bones, when in the cartilaginous state, are composed of it. According to Scherer, it is composed of $C_{48}H_{40}N_6O_{20}$; that is, of proteine + 4HO + O_2. Chondrine leaves, when burned, from 4 to 6 per cent. of ashes, chiefly bone-earth.

Arterial membrane.—The middle coat of the artery, which is a very elastic membrane, leaves, when burned, 1·7 per cent. of ashes. According to Scherer, it is composed of $C_{48}H_{38}N_6O_{16}$; that is, proteine + 2HO.

Horny matter.—This occurs in two forms, *membranous* and *compact.* The former constitutes the epidermis, and the epithelium, or the lining membrane of the vessels, of the intestines, and of the pulmonary cells. The latter forms hair, horn, nails, &c.

Scherer has analysed numerous specimens of both kinds of horny matter, and deduces from his results the formula $C_{48}H_{39}N_7O_{17}$; that is, proteine $+ NH_3 + O_3$.

Horny matter, when acted on by potash, yields proteine on the addition of acetic acid.

Feathers are closely allied to horny matters, but, according to Scherer, contain 1 at. of oxygen less; the formula of feathers, deduced from his analysis, being $C_{48}H_{39}N_7O_{16}$.

Pigmentum nigrum oculi. — This substance, according to Scherer, contains more carbon than any of the preceding; but its formula has not been ascertained.

It is to be particularly observed, that the formulæ above given for the principal tissues of the body are only intended to show the relation they actually bear to proteine. It is not meant that they are formed in the body by the addition of water, ammonia, or oxygen to proteine: on the contrary, we are as yet ignorant of the conditions under which they are produced; and in some cases, as for example in gelatine, several different views may be taken of their formation.

BRAIN AND NERVOUS MATTER.

Nervous matter is distinct from all other animal tissues, and is produced by the animal system exclusively. In composition it is intermediate between fat and the compounds of proteine; containing nitrogen, which is absent in fats, but in far smaller quantity than proteine does; and being, on the other hand, much richer in carbon than proteine, or its compounds. It appears likewise to contain phosphorus as an essential ingredient.

From the recent researches of Frémy, brain appears to contain a peculiar acid, analogous to the fatty acids, which he calls Cerebric acid, and which contains nitrogen and phosphorus; this is mixed with an albuminous substance, with an oily acid—the *oleophosphoric acid*, with *cholesterine*, and finally with small quantities of oleine and margarine, and of oleic and margaric acids.

The two acids, peculiar to the brain and nervous matter, occur sometimes free, but generally combined with soda or with phosphate of lime.

Cerebric acid is extracted by ether from the brain after it has been exposed to the action of boiling alcohol, which coagulates the albumen. The matter deposited on cooling by the ether is a mixture of cerebric acid, generally combined with soda or bone-earth, oleophosphate of soda, and a little albumen.

This mixture is acted on by alcohol, acidulated with sulphuric acid, which precipitates sulphates of lime and soda, and albumen. The filtered solution contains cerebric and oleophosphoric acids; cold ether removes the latter, and the former is purified by solution in hot ether and crystallisation.

When pure, it is white, crystalline, and pulverisable. In hot water it swells up like starch, but does not dissolve. It contains phosphorus, but no sulphur if purified from albumen; the phosphorus amounts to barely 1 per cent.: and it contains 2·3 per cent. of nitrogen. It has the characters of a fatty acid, but its acid properties are feebly marked.

Oleophosphoric acid. — This acid has not yet been obtained quite pure. With the alkalies it forms soaps, and its compound with soda appears to exist in the brain. When it is long boiled with water or alcohol, it is resolved into oleine and phosphoric acid. This change is accelerated by acids, but it takes place also spontaneously at the ordinary temperature, only more slowly; and the presence of animal matter in a state of decomposition seems to cause it to be resolved into oleine and phosphoric acid. Thus, when brain has been allowed to undergo partial putrefaction, it no longer yields oleophosphoric acid, but oleine and phosphoric acid. It contains 2 per cent. of phosphorus. The oleine of this acid is identical with that of human fat.

Cholesterine.—This fat, as extracted from the brain, in which it occurs in considerable quantity, has the same composition and properties as the fat of biliary calculi. (Couerbe; Frémy.) Frémy has also succeeded in detecting in the liver traces of the characteristic fat acids of the brain.

The grey portions of the brain appear to be chiefly albuminous; while the white portions consist of an albuminous tissue, similar to the grey, but loaded with the fats above described.

The softening of the brain in diseases of that organ seems to be the result of putrefaction, and is accompanied by the separation of the oleine from the phosphoric acid. The oleine itself also is decomposed, yielding free oleic acid.

There can be no doubt that the brain and nervous matter (which is quite similar to brain) are formed in the body from compounds of proteine, either by the loss of some azotized compounds, or by the addition of highly carbonised products, such as fat. But we are ignorant in what part of the body, or by what organs, nervous matter is prepared. This point requires minute investigation. In the meantime, according to Chevreul, the fatty matters, which occur in small quantity in the blood, are similar to those of the brain.

Bones. — The bones of animals are composed of bone-earth and gelatinous tissue. By the action of hydrochloric acid the earthy matter is dissolved, and the animal tissue is left. It is soft, retains the form of the bone, and when dried becomes brittle and semitransparent. When boiled with water, it yields a solution of gelatine, fatty matter remaining undissolved.

The earthy matter is formed of a peculiar phosphate of lime, $8CaO + 3P_2O_5 = HO,2CaO,P_2O_5 + 2(3CaO,P_2O_5)$; that is, a compound of two forms of tribasic phosphate. It forms rather more than half the weight of the bone, and contains a variable proportion of carbonate of lime. Fluoride of calcium is sometimes, but not always, present in recent bones; in fossil bones, and in human bones from Herculaneum, it is always found.

Teeth contain the same ingredients as bones, but the proportion of earthy matter is greater, amounting to nearly 70 per cent. The *enamel* of the teeth contains no animal matter, and fluoride of calcium is found in it.

In rickets, the proportion of earthy matter is much diminished. Callus and exostosis are said by Valentin to contain more carbonate of lime than sound bone, and carious bone to contain less.

When bones are heated in the open fire, they leave an earthy skeleton, which is quite white and has the form of the bone. If bones are heated in close vessels, they give off carbonate of ammonia and tarry products, and leave a black mass, which consists of bone-earth, with about 10 per cent. of finely divided charcoal. It is called bone- or ivory-black, and is much used to decolorise organic solutions.

Milk.—This important secretion, destined for the support of the young of the mammalia, is characterised by the caseine it contains. But it also contains certain oily or fatty matters which constitute butter, and which, besides fats analogous to the ordinary animal fats, contain certain volatile acids (see p. 1024), to which the smell and peculiar taste of butter are owing. Milk further contains sugar of milk, or lactine (see p. 935) ; and, when the caseine has been coagulated by an acid, the whey, besides lactine and salts, contains an albuminous matter, which is coagulated by heat.

The composition of milk is such, that it is capable of supporting animal life without any other food. Its caseine and albumen serve for the formation of blood, and for the nutrition of the animal tissues, while its sugar and fat support respiration ; and it furnishes, besides, all the salts which the body requires.

The following table exhibits the composition of the milk of woman, of the ass, and of the cow. (Henry and Chevallier.)

	Milk of		
	Woman.	Ass.	Cow.
Cheese or caseine	1·52	1·82	4·48
Butter	3·55	0·11	3·13
Sugar of milk	6·50	6·08	4·77
Salts and mucus	0·45	0·34	0·60
Water	87·98	91·65	87·02
	100·00	100·00	100·00

When the food is highly farinaceous, the proportion of butter is increased; but when the food contains much of the compounds of proteine, there is less butter and more caseine present. The more active exercise is taken, the smaller also is the proportion of butter.

Milk, after it has become sour, undergoes the vinous fermentation. (See p. 936.)

Saliva.—This fluid, secreted by the salivary glands, is composed of water, with about 1 per cent. of solid matter, partly saline. It often contains a trace of sulphocyanide of potassium, or at least of a salt which strikes a red colour with persalts of iron ; but this might be done by an acetate. The animal matter of saliva has been described under the name of *Salivary matter.* It is soluble in water, and not coagulated by heat.

Saliva possesses, in an eminent degree, the property of frothing with air, like a solution of soap; and Liebig (Animal Chemistry, p. 113) conceives that its use is to introduce in this manner, during mastication, a certain quantity of air into the stomach, the oxygen of which is employed in digestion.

Gastric juice.—This remarkable fluid seems to contain hardly any principle capable of accounting for its solvent power. In the empty stomach it is neutral, but during digestion it becomes acid, from the separation of free muriatic acid. According to Wasmann and other chemists, it contains a peculiar principle, *Pepsine,* which has the property of dissolving food, and which is obtained by the action of water on the well-washed lining membrane of the stomach of the pig. According to Liebig, however, pepsine, as a distinct compound, does not exist. The solution of the lining membrane, slightly acidulated with hydrochloric acid, certainly dissolves albumen and fibrine, if kept in contact with them out of the body at the ordinary temperature. But none of these effects take place, unless the membrane has been previously exposed to the air, *and is in a state of decomposition.* Hence Liebig ascribes (Animal Chemistry, 109 seq.) the solvent power of the gastric juice to the gradual decomposition of a matter dissolved from the membrane, aided by the oxygen introduced in the saliva. Albumen, &c. when thus in contact with decomposing or fermenting matter, are rendered soluble by a new arrangement of their particles. The accumulation of free hydrochloric acid, derived, no doubt, from common salt, at last puts a stop to further change. The whole food is now brought into the form of *chyme*, an opaque homogeneous fluid, which afterwards passes, first into *chyle*, and finally into perfect blood. In the chyle, the formation of fibrine has already taken place; for, when drawn, it coagulates spontaneously, like blood.

Pancreatic juice.—The fluid secreted by the pancreas is poured into the duodenum, and mixes with the chyme as the latter leaves the stomach. It contains albumen, and, according to some, caseine, and is acid. Its nature, however, is little understood, and its uses at present are unknown.

BILE AND BILIARY CALCULI.

The bile is a yellowish green viscid liquid, secreted by the liver. It has a faint disagreeable smell; and its taste is at first sweet, afterwards bitter and nauseous. Ox bile has been chiefly examined, but that of man and other animals is very similar. The researches of Tiedemann and Gmelin, of Berzelius and of Demarçay, have shown that bile may be made to yield a vast number of different compounds, most of which are products of decomposition.

The bile, according to Demarçay, contains soda in combination with a peculiar acid, *choleic acid.* When bile is boiled with an excess of hydrochloric acid, it yields ammonia, *taurine*, and *choloidic acid;* and, when boiled with caustic potash, it yields carbonic acid, ammonia, and *cholic acid.*

Choleic acid.—When bile is acted on by alcohol, certain impurities are left undissolved. The purified bile gives with acetate of lead a precipitate of choleate of lead, which, when acted on by sulphuretted hydrogen, yields choleic acid.

It forms a yellow spongy mass, soluble in water and alcohol, which has an acid reaction and a bitter taste, and is decomposed by heat. It combines with soda, forming a compound which Demarçay considers as a soap, the solution of which in water has the physical characters of bile. But although this be the case, and although the composition of the choleic acid appears to be the same as that of the organic part of bile, yet we cannot consider the bile as choleate of soda; for the latter is decomposed by acetic acid, which has no action on bile.

According to the analyses of Demarçay and Dumas, as calculated by Liebig, the formula of choleic acid is $C_{76}H_{66}N_2O_{22}$, and this formula may represent also the organic part of the bile.

When choleic acid is boiled with hydrochloric acid, it yields ammonia, taurine, and choloidic acid. The latter, being insoluble, is deposited, and the taurine is extracted from the mother liquor by concentrating and adding a large quantity of alcohol, when the taurine slowly crystallises.

Choloidic acid. — This acid is solid, fusible, of a yellow colour and bitter taste, insoluble in water, soluble in alcohol. It combines with bases, neutralising them, and forming salts which are soluble in alcohol. It contains no nitrogen, and its formula is $C_{72}H_{56}O_{12}$.

Taurine.—This substance forms white crystalline needles, which are soluble in water, and sparingly soluble in alcohol. Its formula is $C_4H_7NO_{10}$.

The production of these substances is easily explained.

$$\begin{array}{ll}
\text{If from choleic acid . . . .} & C_{76}H_{66}N_2O_{22}, \\
\left.\begin{array}{ll}\text{We subtract 1 at. taurine .} & C_4H_7NO_{10} \\ \text{And 1 at. ammonia .} & H_3N\end{array}\right\} & =C_4H_{10}N_2O_{10}, \\
\hline
\text{There remains 1 at. choloïdic acid .} & =C_{72}H_{56}O_{12}.
\end{array}$$

Cholic acid.—This acid is formed, along with carbonic acid and ammonia, when bile or choleic acid is boiled with an excess of caustic potash. It is precipitated by acetic acid, and purified by alcohol from unaltered choleic acid.

When pure, it forms fine needles, which are permanent in the air; or large tetraedrons, which become opaque on exposure. It is insoluble in water, soluble in alcohol and ether. It forms neutral salts with bases. Its formula is $C_{74}H_{60}O_{18}$, and its formation is easily explained.

$$\begin{array}{ll}
\text{If from choleic acid . .} & C_{76}H_{66}N_2O_{22}, \\
\left.\begin{array}{lll}\text{We subtract 2 at. carbonic acid .} & C_2 & O_4 \\ \text{And 2 at. ammonia . .} & N_2 & H_6\end{array}\right\} & =C_2H_6N_2O_4, \\
\hline
\text{There remains 1 at. cholic acid .} & =C_{74}H_{60}O_{18}.
\end{array}$$

Berzelius states that the bile is far from being so simple in its constitution as Demarçay supposes; and by a series of ingenious processes has obtained from the bile a number of different substances, which he has named *Biline*, *Biliverdine*, *Dyslysine*, *Fellinic acid*, and *Cholinic acid*, besides taurine and cholic acid, as already described. Biline is essentially the same as Demarçay's choleic acid, and it is probable that most of the others are products of decomposition. But even supposing choleic acid to be composed of two or more different compounds, not isolated by Demarçay, yet, as Liebig has well remarked, (Animal Chemistry, 315,) we must not overlook the fact, that it is constant in its composition, and that from this composition we can deduce the principal products of the action of acids and alkalies on bile. It is choleic acid or bile *as a whole*, whether it be one compound or a mixture of several, to which we have to look for the explanation of the changes by which bile may be formed or decomposed. The researches of Berzelius have rendered it probable that choleic acid is not a single compound; but this does not affect its ultimate composition, nor its relation to decomposing agents. It is also clear that bile is very prone to change in almost all circumstances, and yields a great variety of products, most of which have little physiological interest. For these reasons we shall merely refer the reader to the elaborate paper of Berzelius in the foreign journals. The results of Demarçay we have given more in detail; because, as calculated and interpreted by Liebig, they admit of direct application to physiology.

When dried bile is acted on by alcohol, the pure bile or choleate of soda is dissolved, and the residue is found to contain mucus, salts, and fatty matter. The latter consist of cholesterine and ordinary fat, and possibly contain a portion of the peculiar fats of brain. The dissolved portion, besides true bile, contains a small portion of soaps of margaric and oleic acids with soda.

The sugar of bile or picromel of Gmelin, so called from its sweet and bitter taste, appears to be choleic acid or biline, altered by the processes to which it has been subjected.

Biliary calculi.—The concretions which form in the gall-bladder, and are often the cause of much suffering, are almost always composed of cholesterine, with more or less colouring matter. Hot alcohol dissolves the cholesterine, and deposits it in shining scales on cooling. These calculi have often a form nearly cubical, and a pearly lustre. For the properties and composition of cholesterine, see p. 1083.

Lithofellic acid.—This acid has recently been discovered by Goebel in a biliary concretion, and appears to be the chief constituent of the concretions called *bezoar stones*, which occur in herbivorous animals. According to Ettling and Will, its formula is $C_{40}H_{36}O_8$. It is soluble in hot alcohol, and forms a crystalline powder on cooling. It is insoluble in water, and forms with alkalies soluble soaps, with oxides of lead and silver insoluble compounds. It is decomposed by heat, and when acted on by nitric acid yields a new acid.

According to Liebig, who deduced the above formula from the analysis of Ettling and Will, lithofellic acid may be formed, along with hippuric acid, by the oxidation of choleic acid.

$$\left.\begin{array}{lr} \text{1 eq. choleic acid,} & C_{76}H_{66}N_2O_{22} \\ \text{and 10 eq. oxygen,} \quad . \quad . & O_{10} \end{array}\right\} = \left\{\begin{array}{lr} \text{2 eq. hippuric acid,} & C_{36}H_{16}N_2O_{10} \\ \text{1 eq. lithofellic acid,} & C_{40}H_{36}\quad O_{8} \\ \text{14 eq. water} & H_{14}\quad O_{14} \end{array}\right.$$

$$\overline{C_{76}H_{66}N_2O_{32}} \qquad\qquad \overline{C_{76}H_{66}N_2O_{32}}$$

Excrements.—The excrements of man contain about one-fourth of their weight of solid matter. The ashes of dry fæces amount to 13·58 to 15·00 per cent., and are composed of phosphates and other salts. The excrements also contain nitrogen, and yield ammonia when they putrefy. The value of night-soil as manure depends on the salts and ammonia of the fæces, and also in a great measure on the ammoniacal and other salts of the urine. The colour of fæces is generally said to be owing to bile; but Liebig states that there is only a mere trace of bile, if any, to be found in the fæces either of man or animals. The yellow matter of fæces is insoluble in alcohol, with the exception of a small proportion, and even that has not the characters of bile.

Lymph.—The lymph of cellular membrane is water, with a small trace of albumen and of common salt. The lymph secreted by the serous membranes is much more highly charged, containing 7 or 8 per cent. of albumen and salts. It coagulates when heated, or by the action of nitric acid. The liquor amnii and the fluid of hydatids is similar; but the fluid of dropsy is said to contain urea, and to have cholesterine suspended in it.

Mucus.—This is the secretion of the mucous membranes. When dried, it leaves 6 or 7 per cent. of yellowish solid matter, of which about 5 parts are mucus, the remainder albumen and salts. Mucus does not dissolve in water, but swells like tragacanth into a viscid mass. It dissolves in caustic potash.

Pus is the matter secreted by ulcerated surfaces. When healthy, it is a thick yellowish liquid, formed of opaque globules floating in a clear fluid. When mixed with water, the globules fall, forming a yellow insoluble sediment. Pus contains about 14 per cent. of solid matter, and is coagulated by heat and by acids. It contains albuminous matter, fatty matter, and salts.

The matter of the globules of pus is similar to that of the globules of blood, or globuline. Pus is distinguished from mucus by the microscope, or by the action of caustic potash, with which pus becomes thick and ropy, while mucus forms a thin solution.

URINE AND URINARY CALCULI.

Urine.—This important excretion is separated from the arterial blood in the kidneys. It has a pale yellow colour and a peculiar smell. Its density varies from 1·012 to 1·030. It has an acid reaction, or is neutral, but never alkaline in a state of health.

On standing, it deposits a slimy mucus-like substance, secreted from the lining surface of the bladder. This mucus acts as a ferment, and causes the urine after a time to undergo decomposition; for, when it is separated by the filter, the urine may be kept unchanged for a much longer time.

When spontaneous decomposition has taken place, the urine is alkaline from the presence of carbonate of ammonia, derived from the urea. Urine contains about 7 or 8 per cent. of solid matter, the remainder being water.

The characteristic organic principles of urine are urea and uric acid (see pp. 711 and 759). The urea has been recently declared by Cap and Henry to be combined with lactic acid; but, in repeating their experiments, the editor has always obtained pure urea instead of the lactate. It would appear, therefore, that in some individuals it occurs uncombined, in others as lactate. It is not known precisely in what state of combination the uric acid occurs; but, when it is not deposited spontaneously, it appears on the addition of an acid, and the spontaneous deposition of it is probably owing to the presence of free acid in unusual quantity.

The proportion of urea has been found by Lecanu to be tolerably uniform in the same individual, but to vary much in different persons. It is larger in adult men than in women, and least of all in old people and very young children. The proportion of uric acid varies in a similar way. The following analysis of urine, by Berzelius, will give a view of the usual composition of human urine:

Water	933·00
Urea	30·10
Uric acid	1·00
Lactic acid, lactate of ammonia, and animal matter adhering to them	17·14
Mucus of the bladder	0·32
Sulphate of potash	3·71
Sulphate of soda	3·16
Phosphate of soda	2·94
Phosphate of ammonia	1·65
Chloride of sodium	4·45
Hydrochlorate of ammonia	1·50
Earthy matters, with a trace of fluoride of calcium	1·00
Siliceous earth	0·03
	1000·00

Scharling has recently examined the brown organic matter which gives the colour to inspissated urine, and seems also to be the source of its peculiar odour. He obtained a brown fusible resinous mass, having a strong odour of castoreum when dry, and a urinous smell when boiled with water. He calls it *oxide of omichmyle*, (from *ομιχμα*, urine,) and supposes it to contain a radical, omichmyle, the composition of which is still unknown.

When urine is distilled with an excess of nitric acid, there are formed several products, among which Scharling states that he has observed benzoic acid, and an acid containing chlorine derived from the salts of the urine. This acid appears also to be formed when oxide of omichmyle is distilled with nitromuriatic acid. From his analysis Scharling deduces the formula $C_{14}H_4ClO_3 + HO$, which represents benzoic acid in which 1 eq. of hydrogen is replaced by 1 eq. of chlorine. It is also isomeric with chloride of salicule or chlorosaliculic acid.

Along with this acid there is formed a volatile greenish yellow oil, which Scharling found to contain twice as much chlorine, and the elements of nitric acid. This compound he calls nitro-chloromichmyle. When heated with acids, it is decomposed, and yields another oily matter, chloromichmyle. All these observations require confirmation.

The urine of herbivora is alkaline, and, when the animals are stall-fed, contains, besides urea, hippuric acid; but when they live in the open air, or are forced to labour, benzoic acid alone is found.

The urine of the carnivora is acid, and contains phosphates and sulphates of ammonia and soda, as well as uric acid and urea.

The urine of serpents and of birds is of a soft semisolid consistence, and dries into a mass like chalk. It is almost pure urate of ammonia, but contains a small quantity of phosphates.

Urinary calculi. — The most abundant calculi are those of *uric acid.* They have generally a fawn colour, are soluble in caustic potash, and precipitated from the solution by acids. They also dissolve in nitric acid with the aid of heat; and the solution, when gently evaporated to dryness, leaves a purple stain of murexide. This species of calculus is totally consumed before the blowpipe, leaving a mere trace of ashes.

Urate of ammonia occasionally forms a calculus, which is distinguished from the former by giving out ammonia when digested with potash.

Bone-earth forms a common calculus, which is earthy, soluble in diluted acids, except acetic acid, insoluble in potash, and indestructible by heat.

Ammoniaco-magnesian phosphate also occurs pretty frequently. It is the same double salt which forms whenever magnesia, phosphoric acid, and an excess of ammonia are brought together. It is soluble in acetic acid, and precipitated again by ammonia. It has often a crystalline aspect. When heated, it gives off ammonia, and leaves phosphate of magnesia.

Fusible calculus.—This very common calculus is a mixture of the two preceding. It is white and chalky, and melts easily before the blowpipe. Acetic acid dissolves part of it, hydrochloric acid the rest.

Oxalate of lime, or *Mulberry calculus*, has a dark-coloured rough surface, and is very hard. It is insoluble in acetic acid; but, when heated to redness, it is converted into carbonate of lime, which dissolves in acids with effervescence.

Xanthic oxide is a rare calculus, first observed by Dr. Marcet. It has a light brown colour, and becomes resinous by friction. It dissolves in caustic potash, and is precipitated from the solution by carbonic acid. It dissolves in nitric acid without effervescence; and, when evaporated, leaves a yellow mass. Its formula is $C_5H_2N_2O_2$.

Cystic oxide is also very rare. Discovered by Wollaston. It is yellowish white and crystalline, with a waxy lustre. It dissolves in caustic potash, and is deposited from the solution in hexagonal plates on the addition of acetic acid. It also dissolves in ammonia and the mineral acids; with the latter it forms crystalline compounds. When its solution in potash is heated, ammonia is first given off, and afterwards a combustible vapour, with the odour of sulphuret of carbon. Its formula is $C_6H_6NS_2O_4$.

Both the preceding species are entirely consumed before the blowpipe.

Calculi sometimes occur, in which layers of uric acid alternate with layers of phosphate of lime, ammoniaco-magnesian phosphate, and fusible calculus.

CHANGES WHICH OCCUR DURING THE LIFE, GROWTH, AND NUTRITION OF VEGETABLES AND ANIMALS.

When we consider that the food of vegetables and of animals is either altogether different from their substance, or passes, before being assimilated, into a new form, we cannot hesitate to admit that the nutrition and growth of both classes of organised beings depend on chemical agencies, although these operate under peculiar conditions, and are influenced by the unknown force which we call Vitality, so as to produce results that cannot be imitated by the chemist in his experiments on dead matter.

The food of vegetables, as far as their organic structure is concerned, consists entirely of inorganic compounds; and no organised body can serve for the nutrition of vegetables until it has, by the processes of decay or putrefaction, been resolved into certain inorganic substances.

These are carbonic acid, water, and ammonia, which are well known to be the final products of putrefaction. But, even where these are supplied to vegetables, their growth will not proceed unless certain mineral substances are likewise furnished in small quantity, either by the soil, or in the water used to moisten it. Almost every plant, when burned, leaves ashes, which commonly contain silica, potash, phosphate of lime; often also magnesia, soda, sulphates, and oxide of iron. These mineral bodies appear to be essential to the existence of the vegetable tissues, so that plants will not grow in soils destitute of them, however abundantly supplied with carbonic acid, ammonia, and water.

In the process of germination, oxygen is absorbed, heat is given out, and in some cases at least an acid, said to be the acetic, is formed, the use of which appears to be to extract from the soil the bases necessary for the future progress of the plant. The starch or albumen of the seed becomes soluble, and in the juice undergoes certain changes, by which the woody fibre or lignine, required for the stem and leaves, is produced; but, as soon as leaves and roots are developed, the further nutrition of the plant depends on their power of absorbing from the atmosphere and the soil the matters which constitute the food of the plant.

According to Liebig (see his Agricultural Chemistry), the whole of the carbon is now derived from carbonic acid, which is either absorbed from the atmosphere and rain-water by the leaves, or from the moisture and air in the soil by the roots. Its carbon is retained, and its oxygen given out; this decomposition being effected in the plant at all times when exposed to the action of light, along with a certain temperature.

The hydrogen and oxygen of vegetables are derived from water; and the reader will here observe, that the great mass of vegetables, consisting of lignine, starch, gum, &c. is actually composed of carbon *plus* water.

The nitrogen of vegetables is derived chiefly, if not exclusively, from ammonia, which is supplied to them in rain. Liebig has shown beyond all doubt, that rain-water always contains more or less carbonate of ammonia. If we acidulate pure rain-water with a little sulphuric acid, and evaporate to a small bulk, the addition of lime causes the disengagement of ammonia, easily known by its pungent smell. It is remarkable that the ammonia of rain-water has always a putrid smell, which indicates its origin. In fact, it is derived from the putrefaction of preceding races of animals and vegetables, and must at all times exist in the atmosphere; although its relative quantity is so small, that it is not easily detected until it has been accumulated in rain, which, in passing through the air, dissolves it readily and conveys it to the earth.

It is also to be observed, that the soil itself, like all porous bodies, possesses the property of absorbing ammonia, and therefore will attract it from the atmosphere. Alumina, peroxide of iron, and humus, all absorb ammonia powerfully. Gypsum (sulphate of lime) and other sulphates convert the carbonate of ammonia into the more fixed sulphate, which remains in the soil till absorbed by the roots. This explains in a great measure the use of these ingredients in fertile soils.

It is only under the influence of light that plants can decompose carbonic acid, fixing its carbon and setting free its oxygen. During the night, on the contrary, they undergo a kind of slow combustion, oxygen being absorbed, and carbonic acid formed. But the balance in this curious alternation is vastly in favour of the process by which oxygen is sent into the atmosphere, for, the whole carbon of a forest, for example, being derived from carbonic acid, an equivalent quantity of oxygen must have been liberated; and this consideration alone enables us to explain the fact, that, notwithstanding the enormous amount of oxygen withdrawn from the atmosphere by the respiration of animals, by combustion, by putrefaction, and by the action of vegetables during the night, in all of which processes the oxygen is converted into carbonic acid of equal volume, the proportion of oxygen in the atmosphere does not diminish, and that of carbonic acid does not increase.

From these considerations it appears that there must always exist a balance or fixed proportion between the existing amount of animal and that of vegetable life. Where animals abound, and where men carry on the usual operations of civilised life, there, carbonic acid must be largely formed. But this carbonic acid, in yielding its carbon to vegetation, yields also its oxygen to restore the purity of the air, and support again the respiration of men and animals. Again, the decay and putrefaction of both animals and vegetables yield carbonic acid and ammonia, the very substances which form the food of a new race of vegetables; and these again contribute to the nourishment of new animals; so that, in this unceasing round of chemical changes, the death of one generation supplies the means of life to that which is to follow.

It has long been the prevailing opinion that the carbon of plants is derived directly from humus or humic acid existing in the soil, which is supposed to be absorbed in the form of a solution in water, or as humate of ammonia; but it must be admitted, as Liebig has shown, that there is no evidence whatever that humus is directly absorbed by plants. Humus, as it exists in the soil, is almost entirely insoluble in water, and, when a soluble form occurs, the solution, however weak, is always of a dark brown colour; whereas the juices of plants, when first absorbed, are colourless. Again, humic acid, as described by chemists, never occurs in soils, but is a product of the action of alkalies on humus, and besides forms solutions as dark-coloured as those of humus. Good fertile soil digested with cold water yields to it no colour; water, filtering through such soil, passes colourless, as may be daily observed; nay, moss-water, which is actually coloured brown by humus, is decolorised by passing through a good fertile soil containing humus; finally, a peaty soil, which contains more humus than any other, is notoriously barren.

On the other hand, the first vegetables which grew on the earth could not have derived their carbon from humus, which is a product of the decay of vegetables, but could only have obtained it from carbonic acid; and, if this source of carbon were then sufficient, there is no reason to look for another. Besides, if we reflect on the extreme luxuriance of vegetation in uninhabited countries where the soil has never been manured, we cannot fail to perceive that the carbon of that vegetation must have been chiefly derived from the atmosphere; and when, in addition to this, we find that the proportion of humus in all soils bearing vegetation increases rather than diminishes, in spite of the vast amount of carbon annually accumulated and removed in the crops, we are compelled to adopt the same conclusion.

This latter consideration shows, that the humus and other organic matters in manures do not act directly in furnishing carbon, and that their use chiefly depends on other ingredients. These, as Liebig has demonstrated, are, first, the ammonia they contain or yield by putrefaction; and, secondly, the mineral bodies, such as potash, phosphate of lime, &c. found in their ashes.

But, although there is no evidence that humus is directly absorbed by plants, and the phenomena of peat and mossy soils prove that the soluble forms of humus are unfavourable to vegetation, yet it cannot be doubted that humus or mould, both of the soil and the manures, performs an important function. It slowly and gradually undergoes combustion, yielding a constant and steady supply of carbonic acid in moderate quantity. This is partly absorbed by the roots, and partly rises into the atmosphere to be absorbed by the leaves; but, as the proportion of humus in the soil does not diminish, that which is thus consumed is probably restored to the soil by the secretions or rather excretions from the roots.

Humus also probably acts by absorbing and fixing the ammonia of the atmosphere.

The chief use of manures is, according to the above views, which have been admirably laid down by Liebig in his Agricultural Chemistry, not to supply plants with carbon, but with ammonia and inorganic matters. Every plant requires certain mineral substances, without which it cannot prosper; and a soil is fertile or barren for any given plant, according as it contains these. Thus, the ashes of wheat-straw contain much silica and potash, while the ashes of the seeds contain phosphate of ammonia and magnesia. Hence, if a soil be deficient in any one of these, it will not yield wheat. On the other hand, a good crop of wheat will exhaust the soil of these substances, and it will not yield a second crop till they have been restored, either by manure or by the gradual action of the weather in disintegrating the subsoil. Hence the benefit derived from fallows and from the rotation of crops.

When, by an extraordinary supply of any one mineral ingredient, or of ammonia, a large crop has been obtained, it is not to be expected that a repetition of the same individual manure next year will produce the same effect. It must be remembered, that the unusual crop has exhausted the soil probably of all the other mineral ingredients, and that they also must be restored before a second crop can be obtained.

The salt most essential to the growth of the potato is the double phosphate of ammonia and magnesia; that chiefly required for hay is phosphate of lime; while for almost all plants potash and ammonia are highly beneficial.

From the principles above mentioned we may deduce a few valuable conclusions in regard to the chemistry of agriculture. First. By examining the ashes of a thriving plant, we discover the mineral ingredients which must exist in a soil to render it fertile for that plant. Secondly. By examining a soil, we can say at once whether it is fertile in regard to any plants, the ashes of which have been examined. Thirdly. When we know the defects of a soil, the deficient matters may be easily obtained and added to it, unmixed with such as are not required. Fourthly. The straw, leaves, &c. of any plant must be the best manure for that plant, since every vegetable extracts from the soil such matters alone as are essential to it. This important principle has been amply verified by the success attending the use of wheat-straw or its ashes as manure for wheat, and of the clippings of the vines as manure for the vineyard. Where these are used, no other manure is required. Fifthly. In the rotation of crops, those should be made to follow which require different minerals; or a crop which extracts little or no mineral matter, such as peas, should come after one which exhausts the soil of its phosphates and potash.

Of the chemical manures now so much used, *bone-dust* supplies the phosphates which have been extracted by successive crops of grass and corn, the whole of the bones of the cattle fed on these crops having been derived from the soil; its gelatine also yields ammonia by putrefaction. *Guano* acts as a source of ammonia, containing much oxalate and urate of ammonia with some phosphates. *Night-soil* and *urine*, especially the latter, are most valuable for the ammonia they yield, as well as for phosphates and potash; but are very much neglected in this country, although their importance is fully appreciated in Belgium and China. *Bran* is a very valuable manure, especially for potatoes, as it contains much of the ammoniaco-magnesian phosphate.

Nitrate of soda probably acts by its alkali, replacing potash, but it is possible that its acid may also yield nitrogen to plants, although we possess at present no evidence of this, and indeed no evidence that plants can derive their nitrogen from any other source than from ammonia.

Such is a brief sketch of the general laws of vegetation as at present known, in so far as they are connected with chemistry. Of the changes in the juices of vegetables, by which the numerous products of the vegetable kingdom are formed, we know nothing. The juices of plants contain ammonia and sugar, gum or starch; all the elements are therefore present from which the azotised compounds, albumen, fibrine, and caseine, in other words, proteine, may be formed, and it appears that vegetables alone can produce proteine. Thus the final products of vegetation form the food of animals; the modifications of proteine serving for nutrition properly so called, and the starch, gum, sugar, and oil serving for the support of respiration.

The life of animals is distinguished chemically from that of vegetables by the circumstance, that in the former oxygen is constantly absorbed and replaced by carbonic acid, while in the latter carbonic acid is absorbed, its carbon retained, and its oxygen given out. Consciousness and the power of locomotion are peculiar to animals.

In animals two processes are constantly carried on: that of respiration, by which the animal heat is kept up; and that of nutrition, by which the matter consumed in the vital functions and expelled from the body is restored.

Respiration is essentially a combustion of carbon, which in combining with oxygen is converted into carbonic acid, and at the same time furnishes the animal heat. Liebig calculates that the amount of carbon daily burned in the body of an adult man is about fourteen ounces, and that the heat given out is fully sufficient to keep up the temperature of the body, and to account for the evaporation of all the gaseous matter and water expelled from the lungs.

This carbon is derived in the first place from the tissues of the body, which undergo a constant waste, but ultimately from the food.

In the carnivora, whose food is almost entirely composed of compounds of proteine, albumen, &c. one part is devoted to supply the waste of the tissues, while another portion, or a corresponding amount of previously existing tissue, is decomposed so as to yield the carbon required for respiration. As the tissues can only be decomposed by the exercise of the vital functions, this is the reason why, in the carnivora, an enormous amount of muscular motion is required to furnish the necessary supply of carbon.

On the other hand, the food of the herbivora contains but little of the compounds of proteine, only sufficient to restore the waste of the tissues; while the carbon required for respiration is supplied by the starch, gum, sugar, oil, &c. which form the great mass of their food, and no such amount of muscular motion is required in them as in the carnivora.

It is in the form of bile chiefly that the carbon undergoes combustion. Hitherto, the true function of the bile has been disputed; and by most authors that fluid has been considered as an excretion, intended to be expelled from the body in the fæces. But Liebig has shown that only a small fraction of the whole amount of bile can be detected in any shape in the fæces, and that the bile unquestionably is reabsorbed in the intestinal canal and re-enters the circulation, where it soon disappears; and as the proportion of carbon in the bile is very large, although not sufficient to account for all the carbonic acid given out, there is no reason to doubt that it is gradually consumed by the oxygen of the arterial blood, and converted into carbonic acid and water, which escape by the lungs and skin.

To return to the subject of the animal heat: the food that is required, and hence the appetite, must be proportional to the amount of carbon required to supply the animal heat. Now, in hot climates, where the external cooling is less, less heat is required, the appetite is much more feeble, and the usual food, consisting of fruits and vegetables, contains a far smaller amount of carbon than in cold climates, where the appetite is keen, and the food highly carbonised, such as flesh or even blubber. For the same reasons, warm clothing, by diminishing the loss of heat by external cooling, blunts the appetite; and those who remove from a cold to a warm climate always find that their appetite fails. This is a warning from nature to diminish the amount of food taken; and if it were attended to, and the common but absurd practice of stimulating the appetite by ardent liquors and hot spices abandoned, Europeans might enjoy as good health in the East or West Indies as at home. It is obvious, that, even in Europe, more food is required in winter than in summer. (Animal Chemistry, 23.)

In endeavouring to explain the formation of the bile, it is obviously of no moment whether we derive it from the albumen, fibrine, &c. of the food, or those of the tissues, their composition being identical. Liebig, assuming choleic acid to be the chief organic constituent of the bile, and its formula to be $C_{76}N_2H_{66}O_{22}$, has shown that the half of this formula, added to that of urate of ammonia, $C_{10}N_5H_7O_6$, which gives the sum $C_{48}N_6H_{40}O_{17}$, is equal to the formula of blood or flesh, $C_{48}N_6H_{39}O_{15}$, with the addition of 1 at. water and 1 at. oxygen. (Animal Chemistry, 135, 136.) Again, proteine, $C_{48}N_6H_{36}O_{14}$, *plus* 3 atoms of water, gives the same sum, excepting 1 atom of hydrogen, viz. $C_{48}N_6H_{39}O_{17}$. In this way we can see how the tissues, acted on by oxygen and water, may yield the ingredients of bile and urine. This is the first attempt which has been made to trace chemically the connection between the food, the blood or the tissues, and the secretions or excretions; and showing, as it does, that these questions are capable of elucidation on chemical principles, it must be regarded as the most important idea yet suggested in animal chemistry.

Supposing it to be well-founded, the tissues which are consumed are resolved first into bile and urate of ammonia. The former is secreted from the liver, reabsorbed and burned, as before stated. The latter, in serpents and birds, is expelled unchanged; but in man and quadrupeds, in whom the amount of oxygen inspired is much greater, it is also oxidised, yielding finally carbonic acid, ammonia, and urea.

Should the supply of oxygen in the human subject be insufficient to act on the urate of ammonia, then the uric acid is deposited as gravel or calculus; if the supply of oxygen be somewhat greater, but still deficient, oxalic acid is the result, and mulberry calculus occurs; but, if much exercise be taken and abundance of oxygen supplied, the oxidation of the uric acid is completed, and nothing is left but urea or carbonate of ammonia.

This explains the true cause of uric acid and mulberry calculus to be a deficiency of oxygen; it also explains why uric acid calculus is followed by mulberry calculus in those who remove from the town to the country, where more exercise is taken; and from these considerations we may see how valuable are the results which will flow from a thorough investigation of all departments of animal chemistry.

The urine of the herbivora differs from that of man, in containing, besides urea, hippuric acid when they are at rest or stall-fed, and benzoic acid when they are in full exercise, and when consequently more oxygen is supplied. Liebig has shown, that, if to five times the formula of blood we add 9 atoms of oxygen, we have the elements of 6 at. hippuric acid, 9 at. urea, 3 at. choleic acid, 3 at. ammonia, and 3 at. water; and that, if to five times the formula of blood we add 45 at. oxygen, we obtain the elements of 6 at. benzoic acid, 13½ at. urea, 3 at. choleic acid, 15 at. carbonic acid, and 12 of water. Moreover, 2 at. proteine, with 2 at. of water, contain the elements of 6 at. allantoine (found in the urine of the fœtal calf), and 1 at. choloidic acid, which is supposed to be the same as the meconium.

The bile of the herbivora is much more abundant than that of the carnivora, an ox secreting, according to Burdach, 37lbs. of bile daily. As the waste of matter in the herbivora is but limited, it is obvious that it cannot supply all the bile, and consequently a great part of it must be derived from the starch and other non-azotised constituents of their food, which lose oxygen, and enter into combination with some azotised product of the decomposition of compounds of proteine.

In order to show how this is possible, Liebig points out that the elements of 2 at. proteine, with those of 3 at. uric acid and 2 at. oxygen, amount to the same sum as 6 at. hippuric acid and 9 at. urea; while, if to 5 at. starch we add 2 at. hippuric acid and 2 at. oxygen, the sum is equal to 2 at. choleic acid and 20 at. carbonic acid.

Again, if the elements of proteine and starch, oxygen and water being present, undergo transformation and mutually affect each other, the products of this metamorphosis may be urea, choleic acid, ammonia, and carbonic acid. Thus:

$$
\begin{array}{lcl}
\text{5 at. proteine, } 5\,(C_{48}N_{6}H_{36}O_{14}) & = & C_{240}N_{30}H_{180}O_{70} \\
\text{15 at. starch, } 15\,(C_{12}\;H_{10}O_{10}) & = & C_{180}\;\;H_{150}O_{150} \\
\text{12 at. water, } 12\,(\;\;H\;O\;) & = & \;\;H_{12}\;O_{12} \\
\text{5 at. oxygen, } \;.\;\;.\;\;. & = & \;\;O_{5} \\
\hline
\text{The sum is } \;.\;\;.\;\;. & = & C_{420}N_{30}H_{342}O_{237}.
\end{array}
$$

And

9 at. choleic acid,	$9\,(C_{38}N\ H_{33}O_{11})=C_{342}N_9\ H_{297}O_{99}$
9 at. urea, .	$9\,(C_2\ N_2\ H_4\ O_2\ )=C_{18}\ N_{18}H_{36}\ O_{18}$
3 at. ammonia, .	$3\,(\ N\ H_3\ )=\ N_3\ H_9$
60 at. carbonic acid,	$60\,(C\ O_2\ )=C_{60}\ O_{120}$
The sum is	$=C_{420}N_{30}H_{342}O_{237}$.

The reader will observe that these equations are given, not as representing what is actually proved to occur, but only to show how such changes may be conceived on ordinary chemical principles. But it is to be borne in mind, that all the necessary substances meet in the circulation; proteine and starch from the food, oxygen in the arterial blood, and water is never absent: while the resulting products are the chief constituents of the secretions and excretions; viz. carbonic acid, excreted by the lungs; urea and carbonate of ammonia, excreted by the kidneys; and choleic acid, secreted by the liver. (Animal Chemistry, 150 et seq.)

We have thus seen how the carbon in the form of choleic acid or bile may be obtained in a state most favourable for its oxidation or combustion. But, if the supply of oxygen be deficient, the choleic acid may by a partial oxidation yield hippuric and lithofellic acids, just as we have seen that uric acid, partially oxidised, yields oxalic acid; for 2 at. choleic acid + 10 at. oxygen are equal to 2 at. hippuric acid, 1 at. lithofellic acid, and 14 at. water. Thus one species of biliary calculus, identical with the bezoar stones found in the herbivora, may have an origin similar to that of the mulberry calculus, both arising from a deficient supply of oxygen. (Liebig.)

Soda is necessary to the formation of bile, and is supplied in the form of common salt. Where the supply of soda is defective, the metamorphosis of proteine can yield only fat and urea. If we assume for fat the empirical formula $C_{11}H_{10}O$, then 2 at. proteine, with 12 at. water and 14 at. oxygen, in all $C_{96}N_{12}H_{84}O_{54}$, are equal to 6 at. urea, 6 at. fat, and 18 at. carbonic acid. If we assume fat to be $C_{12}H_{10}O$, a similar result may be traced; and the composition of all fats lies between these two empirical formulæ. Now, it is worthy of observation, that, if we wish to fatten an animal, we must carefully avoid giving much salt in its food. (Liebig.)

As another point of connexion between the products of the metamorphosis of bile and of the constituents of urine, in addition to the possibility already mentioned of both being derived from the oxidation of proteine, it may here be remarked, that 3 at. taurine and 3 at. ammonia are equal to 1 at. uric acid, 1 at. urea, and 22 at. water; and that 1 at. taurine and 1 at. ammonia are equal to 1 at. allantoine and 7 at. water. (Liebig.)

It may further be noted that 1 at. uric acid, 14 at. water, and 2 at. oxygen, correspond to 2 at. taurine and 1 at. urea; or, if 2 at. water be added, to 2 at. taurine and 2 at. carbonate of ammonia. Moreover, 1 at. alloxan and 10 at. water are equal to 2 at. taurine; and 1 at. taurine contains the elements of 2 at. oxalic acid, 1 at. ammonia, and 4 at. water. (Liebig.)

As alloxan is a product of the oxidation of uric acid, and as it has been shown above to be related to taurine, that is, to bile, it would be very important to study its action on the system. It might probably act beneficially in some diseases of the liver. It may be safely administered in considerable quantity. (Liebig.)

In the urine of the carnivora we find soda in moderate quantity, combined with sulphuric and phosphoric acids. This soda was contained in their food, and, after contributing to form the bile, has been excreted by the kidneys. But it is never sufficient to neutralise the acids produced, and consequently we find much ammonia along with it, while the urine is acid.

But in the urine of the herbivora soda is present in far larger quantity, and combined with carbonic, hippuric, or benzoic acid. This shows that the herbivora require a far greater amount of soda than is contained in the amount of blood daily consumed, which in them is small; and this soda is obtained from their food, and employed in producing their abundant bile.

The plants on which the herbivora feed cannot grow in a soil destitute of alkalies; but these alkalies are not less necessary for the support of the animals than of the plants. The soda is found in the blood and bile; and the potash is now known to be absolutely essential to the production of caseine, that is, the secretion of milk. In like manner, the phosphate of lime, which is essential to the growth of grasses, is equally essential to the production of bone in the animals which feed on these plants. It is impossible not to be penetrated with admiration of the wisdom which is shown in these beautiful arrangements.

Let us now consider the changes which the food undergoes in the process of digestion, and we shall observe this process in the carnivora, where it is most simple, as their food is identical in composition with their tissues.

When the food has entered the stomach, the gastric juice is poured out, and after a short time the whole is converted into a semifluid, homogeneous mass, the chyme. Many researches have been made to discover the solvent contained in the gastric juice, but in vain. It contains no substance which has the property of dissolving fibrine, albumen, &c.; and we are compelled to adopt the opinion of Liebig, according to which the food is dissolved in consequence of a metamorphosis, analogous to fermentation, by which a new arrangement of the particles is effected. As, in fermentation, the change is owing to the presence of a body in a state of decomposition, or motion which is propagated from the ferment to the sugar by contact; so, in digestion, the gastric juice contains a small quantity of a matter derived from the lining membrane of the stomach, which is in a state of progressive change, and the change or motion is propagated from this to the particles of the food under certain conditions, such as a certain temperature, &c.

The phenomena of artificial digestion confirm this view. If the lining membrane of a stomach, perfectly clean and fresh, be infused in water feebly acidulated with hydrochloric acid, the liquid acquires no solvent action on albumen; but if the membrane be exposed to the air for some time, or be left in water for a while,—in short, if decomposition be allowed to commence,—then the infusion, if coagulated albumen or fibrine be placed in it, and the whole kept at the temperature of the body, by degrees effects a perfect solution or digestion.

Prout has shown that the gastric juice contains free hydrochloric acid. This is derived from the common salt, the soda of which combines with the albumen or fibrine, while its acid, being set free, at length by its accumulation checks further change. Besides the gastric juice, the only other substance employed in digestion is the oxygen which is introduced into the stomach with the saliva, which from its viscidity encloses a large quantity of air. The chyme then leaves the stomach, and gradually passes into the state of chyle, which resembles blood, except in colour, being already alkaline, not acid like the chyme.

By means of the circulation oxygen is conveyed in the arterial blood to every part of the body. This oxygen, acting on the tissues destined to undergo change, produces a metamorphosis, by which new soluble compounds are formed. The tissues thus destroyed are replaced by the new matter derived from the food.

Meantime, those of the products of metamorphosis which contain the principal part of the carbon are separated from the venous blood in the liver, and yield the bile; while the nitrogen accumulates, and is separated from the arterial blood in the kidneys in the form of urea or uric acid.

It has been already mentioned that vegetables alone possess the power of forming proteine, which they furnish to animals in the forms of albumen, fibrine, and caseine. In the animal body these forms of proteine are employed to yield the different tissues, most of which bear a simple relation to proteine. Thus,

Fibrine, albumen, caseine, are	$Pr+S+P+$ salts.
Arterial membrane is	$Pr+2HO$.
Chondrine is	$Pr+4HO+O_2$.
Hair, horn, &c. are	$Pr+NH_3+O_3$.
Gelatinous tissues are	$2Pr+3NH_3+HO+O_7$.

It is not meant that these formulæ express the actual constitution of the tissues, but only that they give the proportion of the elements actually present, and show how they might give rise to the tissues. Some of these tissues contain proteine, or at least yield it when acted on by potash: this is the case with hair and horn. But others, as, for example, the gelatinous tissues, although doubtless derived from proteine, do not contain it, and consequently cannot yield any of its modifications. This explains the fact that gelatine alone cannot support animal life. It cannot yield blood or muscular fibre, although it may serve to nourish the gelatinous tissues. (See *Gelatine.*)

Liebig has shown (Animal Chemistry, p. 141), that gelatine may be formed from proteine in two ways; either by adding to 2 at. proteine 3 at. allantoine and 3 at. water (which are equal to 1 at. uric acid, 1 at. urea, and 4 of water), or by subtracting from 3 at. proteine $\frac{1}{2}$ at. choloidic acid, and adding 4 at. water. These statements apply to Mulder's formula for gelatine; but, as the true formula is still doubtful, they are only mentioned to show the method by which we may hope to arrive at accurate results.

There is another constituent of the animal body, namely fat, the production of which deserves notice. It is not an organised tissue, but is formed and collected in the cellular tissue under certain circumstances. These are rest and confinement, that is, a deficiency of oxygen; and an abundance of non-azotised food. Carnivorous animals are never fat; and the herbivora only become so in confinement.

Now the chief source of fat is starch, or sugar, the composition of which is such, that, if deprived of oxygen, fat remains. If from starch, $C_{12}H_{10}O_{10}$, we take 9 at. oxygen, there remains $C_{12}H_{10}O$, which is one of the empirical formulæ for fat. Or if from starch we remove 1 at. carbonic acid, CO_2, and 7 at. of oxygen, the remainder, $C_{11}H_{10}O$, represents the other empirical formula of fat. We have already seen how fat may be derived from proteine when soda is deficient; and we may here add, that all the elements of food contain more oxygen than fat, in proportion to the carbon. Thus, in albumen, fibrine, and caseine, for 120 eq. of carbon there are contained 36 eq. of oxygen; in starch, for 120 eq. carbon, 100 eq. oxygen; in sugar and gum, 110 eq. oxygen; in sugar of milk, 120 eq.; and in grape-sugar, 140 eq. oxygen; while in fat there are only 10 eq of oxygen for 120 eq. carbon.

It is obvious, therefore, that fat can only be formed by a process of deoxidation. But we have seen that it is produced where oxygen is deficient; and it appears, as Liebig has pointed out, that, when there is a deficient supply of oxygen, the production of fat, which is the consequence of this deficiency, yields a supply of that element, and thus serves to keep up the animal heat and the vital functions, which would otherwise be arrested. This is another beautiful instance of contrivance, equally simple and wonderful.

That fat must be formed by the deoxidising process above alluded to, is proved by the phenomena of the fattening of animals. A goose, tied up, and fed with farinaceous food, altogether destitute of fat, acquires in a short time an increase in weight of several pounds, the whole of which is fat. Again, the bee produces wax, a species of fat, from pure sugar.

With regard to the production of nervous matter, which animals alone can form, we see, from its composition, intermediate between that of proteine and fat, that it may be formed, either by depriving proteine of some azotised product, or by adding to fat an azotised compound. Where it is formed, we do not know; but it must be formed in the animal body: and Liebig has suggested that the power of the vegetable alkalies to affect the nervous system may be owing to their composition, which approaches nearer to that of nervous matter than any other compounds. These alkalies may promote or check the formation of nervous matter, and thus produce their peculiar effects.

In like manner, certain vegetable products analogous to the vegetable alkalies, such as caffeine (or theine) and theobromine, may be supposed, according to Liebig, to promote the secretion of bile, their composition being related to that of some of the products of bile.

Thus 1 at. caffeine (or theine), with 9 at. water and 9 at. oxygen, may yield 2 at. taurine. Again, 1 at. theobromine, with 22 at. of water and 16 of oxygen, corresponds to 4 at. taurine and 1 at. urea; or 1 at. theobromine, 8 at. water, and 14 at. oxygen contain the elements of 2 at. taurine and 1 at. uric acid. (Animal Chemistry, 180.)

Now, it is surely very remarkable that the vegetables containing these compounds, tea, coffee, and cocoa, should be, one or other of them, used by almost all nations to yield a refreshing drink; and it is still more curious that the peculiar principle of tea should turn out to be identical with that of coffee, as recent researches have demonstrated.

We may suppose, with some degree of probability, that where the formation of bile, and consequently that of urine, which is connected with it, does not go on as it ought, the use of these beverages, by promoting the secretion of bile, may assist the process of respiration, promoting the animal heat, and at the same time contributing to the due performance of all the vital functions. At all events, neither the beneficial and refreshing effects of these articles of diet, nor their relation to bile and urine, can be overlooked; and the universal adoption of the practice of using tea, coffee, or chocolate, is a proof that men have discovered and obtained from different sources the means of producing the same effect.

The preceding observations are sufficient to show that we may expect in progress of time to explain the action of all remedies on chemical principles. The true path has been opened up, and it only remains for experimenters to pursue it with energy and perseverance.

In the foregoing pages we have given only a very brief, imperfect, and condensed view of the principal facts recently ascertained in physiological chemistry, with the conclusions to which they naturally lead. Our space is too limited to permit us to do more than this; and, indeed, to have entered more fully into this interesting subject would have been inconsistent with the character of an elementary work.

Enough has been done, however, to convince the reader that the practical applications of the modern organic chemistry are not less important than those which have been so happily made of the more early developed inorganic chemistry. We are only at the commencement of a period, which promises to be richer in valuable discoveries, and in applications to the benefit of mankind, than any which had preceded it.

Those who wish to become more intimately acquainted with the present state of physiological chemistry are referred to Liebig's "Agricultural Chemistry" and to his "Animal Chemistry;" works which have led the way in these most important investigations, and the effect of which on the progress of discovery will long be felt.

PART IV.

ANALYTICAL CHEMISTRY.

(I am deeply indebted to Mr. Parnell for the Sections on Analysis, which he kindly undertook to furnish at my request; and would beg to refer the reader, who is desirous of more detailed instructions, to a very excellent treatise on Chemical Analysis, recently published by that gentleman.— W. G.*)

The subject of Chemical Analysis is so comprehensive, that to give more than a general outline of this branch of practical chemistry would be inconsistent with the plan of these Elements.

The few following observations are thrown into four sections: the first of which comprises general instructions concerning the manipulations necessary in analytical processes; the second contains a few directions for the performance of qualitative analysis; the third, for the quantitative estimation of the most common constituents of minerals; and the fourth, for the analysis of mineral waters.

An analysis may have for its object the estimation of the weights of either the ultimate or proximate constituents of a substance; that is, of the ultimate elements of which a body is composed, without reference to the manner in which those elements are arranged; or of the proximate compounds which form, by their immediate union, the substance in question. In inorganic analysis, the proximate constituents are the substances generally sought; and the elementary composition of these being already known, the ultimate elements of which the substance analyzed is composed are also ascertained.

Before the composition of a substance can be determined quantitatively, it is necessary to have the nature or quality of the constituents accurately determined: and thus a chemical analysis is resolved into two distinct examinations; first, for the nature of the constituents, which is called the *qualitative analysis;* and second, for the respective weights of these constituents, which is the *quantitative analysis.* As an example, it might be ascertained merely that crystallized sulphate of magnesia is composed of magnesia, sulphuric acid, and water; or that the salt mentioned contains, in 100 parts, 16·7 of magnesia, 32·4 of sulphuric acid, and 50·9 of water.

---

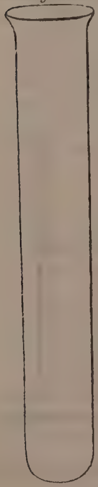
* London: Taylor and Walton, 1842.

SECTION I.

MANIPULATIONS IN ANALYTICAL PROCESSES.

In qualitative analysis the presence of any particular ingredient in the substance under examination is generally ascertained by mixing a test-liquid with the solution of the substance operated on, and observing, by the occurrence or non-occurrence of a precipitate, whether the suspected substance is present or not. If the test-liquid which is added produces no precipitate with any other substance whatever than that sought for, this simple operation is conclusive as to the presence or absence of the suspected body: but if, on the other hand, a test-liquid can produce a precipitate with more than a single substance, it becomes necessary to apply other tests before positive evidence of the presence of a particular substance is obtained. For example, if a neutral solution is to be tested for sulphuric acid, a solution of nitrate of baryta or chloride of barium is added to the liquid: the absence of a precipitate in that case is conclusive as to the absence of sulphuric acid. But if a precipitate occurs, it might be produced in a neutral solution by other acids besides sulphuric; namely, boracic, phosphoric, hydrofluoric, arsenic, and a few others. The precipitates, however, which are produced by these acids in solutions of salts of barytes, are soluble in nitric or hydrochloric acid, while sulphate of barytes is not. If either nitric or hydrochloric acid, therefore, is added to the mixture with the barytic salt containing the precipitate, the solubility or insolubility of the latter shows whether or not it contains sulphuric acid.

Fig. 20.



The mixture of the solution of the substance to be analyzed with the test-liquid may be made either in a conical wine-glass, or in a test-tube. The wine-glass should be provided with a spout for the convenience of pouring liquids into a tube or flask, with the view of applying heat; an operation frequently necessary. Instead of a wine-glass, a test-tube (*fig.* 20) is frequently employed, which possesses the advantage of allowing heat to be applied without transferring the liquid to another vessel. A convenient size for ordinary use is four inches in length, by two-thirds of an inch in diameter.

When it is necessary to examine the action of a test-liquid on a precipitate obtained in the course of testing, that may sometimes be done in the same glass or tube; but often it is requisite to separate the precipitate wholly from the solution, which is accomplished by *filtration*. The process of filtering is one on which the success of analyses, both qualitative and quantitative, but especially of the latter, materially depends.

Filtration is effected by means of a paper filter, formed by doubling twice a circular piece of filtering paper, so as to form a quadrant, and then opening one of the folds, as shown in *fig.* 21. The filter is supported in a glass funnel, which is itself held in any convenient manner; a vessel being placed below the funnel to receive the filtered liquid. Before pouring the turbid liquid on it, the filter should be wetted with a few drops of distilled water, which has the effect of swelling the fibres of the paper, without which precaution the liquid would not at first pass through clear. As the loss of a single drop of the liquid might, in quantitative analysis, render the operation worthless, its transference to a filter must always be directed by a glass rod, applied to the lip of the containing vessel, and held nearly perpendicular, with its extremity very near, but not touching the filter (see *fig.* 22).

Fig. 21.

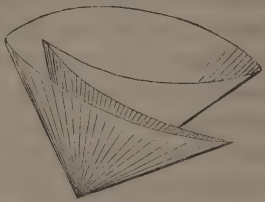
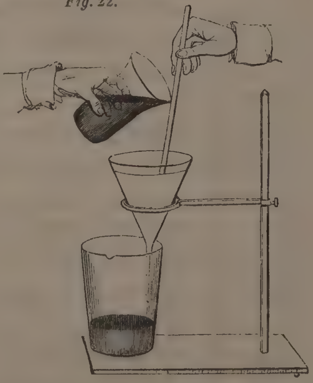


Fig. 22.



In quantitative analysis, the substance, whose weight is to be determined, is generally separated from the solution in which it is contained, by precipitation in a solid form, which is capable of being weighed, and which contains a known proportion of the substance to be estimated. If, for example, the amount of copper contained in a solution is required, that metal is precipitated in the state of oxide by caustic potassa: when washed and perfectly dried, the precipitated oxide may be weighed; and as it is known to contain, in 100 parts, 79·83 parts of copper, the quantity of the metal contained in any amount of the oxide is readily learned by calculation.

The whole of the precipitate having been collected on the filter, as already described, it is washed with pure distilled water until every trace of the original liquid is removed, and then dried on the filter in a hot drying-stove at any temperature below 212°. When dry, if the substance is not decomposed by being heated to redness, it is held, being still on the filter, immediately over a porcelain or platinum crucible, the weight of which when empty is already known; the paper is set on fire, and the precipitate is allowed to fall into the crucible, together with the ash of the filter. The crucible should be placed over a piece of highly-glazed coloured paper, to retain any particles of the precipitate which may fall on it, and which are afterwards carefully put into the crucible. After the matter has been heated to redness, if the filter has been completely burned, the crucible with its contents is weighed, and the weight of the empty crucible is deducted from the entire weight. The ash of the filter also, the average weight of which is determined by previous experiments, must be subtracted from the weight of the heated mass.

In those cases in which the precipitate to be weighed cannot be heated to redness without suffering decomposition, the filter in which it is to be collected should be carefully dried, and introduced, folded, into a platinum crucible, which is then covered and weighed. The necessity of weighing the filter in a closed vessel arises from the circumstance, that dry paper rapidly absorbs hygrometric moisture from the air, which would prevent its weight being accurately determined if placed, open, on the pan of the balance. Having weighed the filter and crucible, the filtration may be conducted as usual; and, when the precipitate is washed and dried in the drying-stove, the filter containing it is folded, introduced into the same crucible, and weighed. After the first weighing, the crucible should be uncovered and exposed to as high a temperature as paper will support without charring, to discover if any loss in weight is experienced through the escape of water, from the mass not having been previously rendered perfectly dry. The weight of the empty crucible and filter, deducted from the entire weight, gives that of the precipitate.

Such is an outline of the methods usually followed in determining the weights of the ingredients of compound bodies. There are, however, many cases in which a different course is pursued, varying according to the nature of the substances and the degree of nicety required; but a description of these would improperly encroach on space which is devoted to another purpose.

SECTION II.

QUALITATIVE ANALYSIS.

In analytical processes the first object is to obtain the substance in a proper state of solution. If soluble in water, that fluid is preferred to every other menstruum; but, if not, an acid or any convenient solvent may be employed. In many instances, however, the substance to be analyzed resists the action even of acids, and in that case the following method is adopted:—The compound is first crushed by means of a hammer or steel mortar, and is afterwards reduced to an impalpable powder in a mortar of agate; it is then intimately mixed with three, four, or more times its weight of potassa, soda, baryta, or their carbonates; and, lastly, the mixture is exposed in a crucible of silver or platinum to a strong heat. During the operation, the alkali combines with one or more of the constituents of the mineral; and, consequently, its elements being disunited, it no longer resists the action of the acids.

The following brief observations on qualitative analysis have reference to the discovery of the constituents of a salt soluble in water, and which consists of a single acid and a single base, to ascertain which two distinct operations are in general necessary.

The bases, for the detection of which means are pointed out, are the following:

1. Oxide of copper.
2. Oxide of lead.
3. Protoxide of tin.
4. Peroxide of tin.
5. Peroxide of iron.
6. Protoxide of iron.
7. Oxide of chromium.
8. Protoxide of manganese.
9. Oxide of zinc.
10. Alumina.
11. Magnesia.
12. Lime.
13. Strontia.
14. Baryta.
15. Ammonia.
16. Potassa.
17. Soda.

1. A portion of the solution of the substance under examination is strongly acidified by a mineral acid, and saturated with sulphuretted hydrogen gas, or else is mixed with water strongly impregnated with that gas.

If a black or brownish black precipitate is formed, the base is one of the first three in the list, namely, oxide of copper, oxide of lead, or protoxide of tin. To distinguish these three bases, add to other portions of the original solution the three following special tests:

(*a.*)—Ammonia; which gives an intense blue liquid with solutions of *copper.*

(*b.*)—Iodide of potassium; which produces a fine yellow precipitate of iodide in solutions of *lead.*

(*c.*)—Bichloride of mercury; which gives with solutions of *proto-salts of tin*, first a white precipitate of calomel, and afterwards a black precipitate of metallic mercury. The solution supposed to contain a proto-salt of tin should be added gradually to the bichloride of mercury, and not in the reverse order, so that the bichloride is at first in large excess.

If a yellow or milky-white precipitate is produced by sulphuretted hydrogen, the base may be either peroxide of tin or peroxide of iron: the precipitate in the former case being the bisulphuret of tin; and in the latter, free sulphur, proceeding from the decomposition of sulphuretted hydrogen by peroxide of iron, the latter being at the same time reduced to the state of protoxide.

(*a.*)—If the base is *peroxide of iron*, yellow prussiate of potash gives, with the original solution, a deep blue precipitate of Prussian blue.

(*b.*)—If the base is peroxide of tin, caustic potassa produces in the original solution a white precipitate of peroxide of tin, which may redissolve in an excess of the alkali, and which, if collected and ignited strongly, becomes insoluble in acids.

2. If sulphuretted hydrogen produces no precipitate in the acid solution of the substance, render another portion of the solution alkaline by ammonia, and then add an excess of hydrosulphuret of ammonia.

(*a.*)—The formation of a black precipitate by hydrosulphuret of ammonia indicates the presence of *protoxide of* *iron*, in which case the original solution gives a deep blue precipitate with the red prussiate of potash.

(*b*.)—If hydrosulphuret of ammonia gives a dull green precipitate, the base is *oxide of chromium*. If the precipitate is collected and fused with a bead of microcosmic salt before the blowpipe, the bead is found to be red while hot, but green when cold.

(*c*.)—If hydrosulphuret of ammonia gives a flesh-colour precipitate, the base is *manganese;* in which case a solution of chloride of lime produces in the original solution a dark brown precipitate of hydrated peroxide of manganese.

(*d*.)—If hydrosulphuret of ammonia gives a white precipitate, the base may be either *oxide of zinc* or *alumina*. These substances may be distinguished by ammonia, which added to the original solution produces a white precipitate in both cases; but oxide of zinc is soluble in excess of the alkali, while alumina is not.

3. If neither sulphuretted hydrogen nor hydrosulphuret of ammonia produces a precipitate, add a solution of carbonate of soda to another portion of the solution. The occurrence of a precipitate shows, that the base is either magnesia, lime, strontia, or baryta, to distinguish which the original solution is tested in the following manner:

(*a*.)—If a solution of oxalate of ammonia gives no precipitate, the base is *magnesia*.

(*b*.)—If oxalate of ammonia gives a precipitate, but dilute sulphate of soda does not, the base is *lime*.

(*c*.)—If dilute sulphate of soda gives a precipitate, the base is either *baryta* or *strontia*. These earths may be distinguished by a solution of hyposulphite of soda, which precipitates baryta, but not strontia.

4. If carbonate of soda gives no precipitate, the base is then one of the three alkalies, ammonia, potassa, or soda.

(*a*).—If *ammonia*, the odour of that alkali is recognized on adding caustic potassa.

(*b*.)—A strong solution of tartaric acid gives a white crystalline precipitate of bitartrate of potassa if the base is *potassa*.

(*c*.)—Salts of *soda* are best distinguished by the yellow colour which they communicate to the flame of alcohol.

The base of the salt having been discovered, the examination for the acid may then be performed. The acids, for the detection of which instructions are given, are the following:

1. Carbonic.
2. Sulphurous.
3. Hydrosulphuric.
4. Hydriodic.
5. Sulphuric.
6. Phosphoric.
7. Arsenic.
8. Boracic.
9. Hydrofluoric.
10. Iodic.
11. Hydrochloric.
12. Nitric.
13. Chloric.

1. To the saturated solution of the salt in water, if soluble, or to the dry salt, if insoluble, dilute sulphuric acid is applied. The effervescence of a gas may proceed from carbonic, sulphurous, or hydrosulphuric acid. A developement of free iodine may proceed from hydriodic acid.

Carbonic.—The gas evolved is inodorous, and, when passed through lime-water, causes a white precipitate, which dissolves on transmitting an excess of the gas.

Sulphurous.—The evolved gas has the pungent smell of burning sulphur.

Hydrosulphuric.—The gas has a fœtid odour, and the solution of the substance produces a black precipitate in salts of lead.

Hydriodic.—To detect hydriodic acid (iodides), mix the solution of the substance with a little solution of starch, and allow chlorine gas to fall on the surface of the liquid: the blue iodide of starch is formed. (See page 300.)

2. If sulphuric acid produces neither effervescence nor developement of free iodine, add a solution of nitrate of baryta to the neutral solution of the substance. The acids which may be precipitated thereby are the following:

Sulphuric.—The precipitate is insoluble in pure hydrochloric acid.

Hydrofluoric.— The powdered substance, gently heated with oil of vitriol in a platinum crucible, evolves a vapour which corrodes glass.

Arsenic (*Arsenious*).—Sulphuretted hydrogen gas, passed through the solution of the substance, strongly acidified by hydrochloric acid, gives a yellow precipitate of sulphuret of arsenic. This precipitate being dried, mixed with black flux, and heated to redness in a glass tube, gives a sublimate of metallic arsenic.

Phosphoric.—Nitrate of silver gives, with the neutral solution of the substance, a yellow precipitate of phosphate of silver, soluble in nitric acid.

Boracic.—If the dry substance is moistened with oil of vitriol, and then alcohol added, the latter burns with a green flame.

Iodic.—Sulphurous acid developes free iodine in the original solution; the presence of iodine may then be ascertained by its action on starch.

3. If dilute sulphuric acid produces no effervescence, and nitrate of barytes no precipitate, the acid may be hydrochloric, hydriodic, nitric, or chloric; in which case add nitrate of silver to the solution of the substance.

(*a.*)—If a yellow precipitate is formed, the acid may be *hydriodic,* which is known by the insolubility of the precipitate (iodide of silver) in solution of ammonia.

(*b.*)—If a white curdy precipitate is formed by nitrate of silver, the acid is *hydrochloric;* in which case the precipitate (chloride of silver) is readily dissolved by ammonia.

4. If nitrate of silver produces no precipitate, the acid is either *nitric* or *chloric.* To detect nitric, add the dry substance under examination to a mixture of protosulphate of iron and oil of vitriol; immediately, or on heating, a brown colour is developed, owing to nitric oxide.

To detect chloric acid, add oil of vitriol to the dry salt: peroxide of chlorine is evolved, and the liquid bleaches vegetable colours.

QUALITATIVE ANALYSIS OF GASES.

Table exhibiting the distinctive properties of oxygen, nitrogen, protoxide of nitrogen, deutoxide of nitrogen, hydrogen, carbonic oxide, and carbonic acid.

(From Graham's Elements of Chemistry.)

	Gases.	
Soluble in water	Carbonic acid	Solution disturbs lime-water.
	Protoxide of nitrogen	Does not.
Support combustion	Oxygen	
	Protoxide of nitrogen	
Combustible	Carbonic oxide	Product of combustion disturbs lime-water.
	Hydrogen	Does not.
Extinguish combustion	Deutoxide of nitrogen	Forms brown fumes with oxygen.
	Nitrogen	Does not.

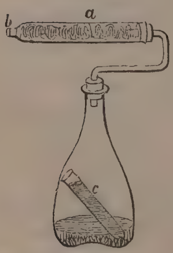
SECTION III.

QUANTITATIVE ANALYSIS.

The following observations on Quantitative analysis relate chiefly to those earthy minerals with which the beginner usually commences his labours, the most common constituents of which are silica, alumina, iron, manganese, lime, magnesia, potassa, soda, and carbonic and sulphuric acids.

Analysis of marble, or carbonate of lime.—The quantity of carbonic acid contained in marble and all other carbonates which are soluble in hydrochloric or sulphuric acid in the cold may be determined by the following simple method :—A known weight of the powdered substance is introduced into a flask similar to that represented in *fig.* 23. The flask should be thin at the bottom to allow of the application of heat, and have the capacity of three or four ounces of water. It is fitted with a cork, which has a perforation to admit a small bent tube; and the latter is connected by means of another cork with a somewhat larger tube, *a*, containing fragments of dry chloride of calcium. The extremity *b* of this tube is drawn out so as to be capillary. The small tube *c* within the flask, sealed at one end, is intended to hold hydrochloric or sulphuric acid to decompose the carbonate, and is of such length that it will not fall flat on the bottom of the flask, but rests against the side at an angle of about 45° with the bottom; so that, on inclining the flask, all the acid contained in this tube can be made to flow out. The apparatus being arranged, the weighed carbonate is introduced into the empty flask with about half an ounce of water; the small tube *c*, containing sufficient hydrochloric or sulphuric acid to decompose the carbonate, is then introduced, taking care that no acid comes in contact with the carbonate, and the flask is closed by the cork attached to the chloride of calcium tube *a*. The whole apparatus is now weighed; after which the flask is inclined, in order that a little of the acid in the tube *c* may flow out and come in contact with the carbonate, which is repeated until the latter is completely de-

Fig. 23.



composed. As the evolved carbonic acid gas is dried in passing through the chloride of calcium tube *a*, nothing else than this gas escapes, and the loss in weight of the apparatus at the close of the experiment is the weight of the carbonic acid required; but, as the flask is then full of carbonic acid gas, which is considerably heavier than air, it should not be weighed in its present state. To get rid of the remaining carbonic acid, the flask is very gently heated, so as to fill it with aqueous vapour, and thus drive out the gas, the steam itself not proceeding further than the chloride of calcium tube. On the condensation of the steam, air enters the flask, which, when cold, is in the same condition as it was when weighed before the decomposition of the carbonate, excepting only in the loss of carbonic acid.

Separation of Lime and Magnesia.—The more common kinds of carbonate of lime frequently contain traces of siliceous and aluminous earths, in consequence of which they are not completely dissolved in dilute hydrochloric acid. A very frequent source of impurity is carbonate of magnesia, which is often present in such quantity that it forms a peculiar compound called *Magnesian limestone.* The analysis of this substance, so far as respects carbonic acid, is the same as that of marble. The separation of the two earths may be conveniently effected in the following manner:—The solution of the mineral in muriatic acid is evaporated to perfect dryness in a flat dish or *capsule* of porcelain; and, after redissolving the residuum in a moderate quantity of distilled water, a solution of oxalate of ammonia is added as long as a precipitate ensues. The oxalate of lime is then allowed to subside, collected on a filter, dried, and decomposed by a red heat; and after moistening the resulting carbonate with a strong solution of carbonate of ammonia, in order to supply any particles of quicklime with carbonic acid, it should be dried, heated to low redness, and regarded as pure carbonate of lime. To the filtered liquid, containing the magnesia, a mixture of pure ammonia and phosphate of soda is added, when the magnesia is precipitated in the form of the ammoniaco-phosphate. Of this precipitate, heated to redness, 100 parts, according to Stromeyer, correspond to 37 of pure magnesia.

The precipitation of magnesia by means of phosphoric acid and ammonia, though extremely accurate when properly performed, requires several precautions. The liquid should be cold, and either neutral or alkaline. The precipitate is dissolved with great ease by most of the acids; and Stromeyer has remarked, that some of it is held in solution by carbonic acid, whether free, or in union with an alkali. The absence of carbonic acid should therefore always be insured, prior to the precipitation, by heating the solution to 212°, acidulating at the same time by hydrochloric acid, should an alkaline carbonate be present. Berzelius has also observed, that, in washing the ammoniaco-magnesian phosphate on a filter, a portion of the salt is dissolved as soon as the saline matter of the solution is nearly all removed; that is to say, it is dissolved by pure water. Hence the edulcoration should be completed by water, which is rendered slightly saline by hydrochlorate of ammonia.

Earthy Sulphates. — The most abundant of the earthy sulphates is that of lime, the analysis of which is easily effected. By boiling it for fifteen or twenty minutes with a solution of twice its weight of carbonate of soda, double decomposition ensues; and the carbonate of lime, after being collected on a filter and washed with hot water, is heated to low redness and weighed.

Of the dry carbonate, fifty parts correspond to twenty-eight of lime. The alkaline solution is acidulated with hydrochloric acid, and the sulphuric acid thrown down by chloride of barium. From the sulphate of baryta, collected and dried at a red heat, the quantity of acid may easily be estimated.

The method of analyzing the sulphates of strontia and baryta is somewhat different. As these salts are difficult of decomposition in the moist way, the following process is adopted:—The sulphate, in fine powder, is mixed with three times its weight of carbonate of soda, and the mixture is heated to redness in a platinum crucible for the space of an hour. The ignited mass is then digested in hot water, and the insoluble earthy carbonate collected on a filter. The other parts of the process are the same as the foregoing.

Mode of analyzing Compounds of Silica, Alumina, and Iron.— Minerals, thus constituted, are decomposed by an alkaline carbonate, at a red heat, in the same manner as sulphate of baryta. The mixture is afterwards digested in dilute hydrochloric acid, by which means all the ingredients of the mineral, if the decomposition is complete, are dissolved. The solution is next evaporated to dryness, the heat being carefully regulated towards the close of the process, in order to prevent any of the chloride of iron, the volatility of which is considerable, from being dissipated in vapour. By this operation, the silica, though previously held in solution by the acid, is entirely deprived of its solubility; so that, on digesting the dry mass in water acidulated with hydrochloric acid, the alumina and iron are taken up, and the silica is left in a state of purity. The siliceous earth, after subsiding, is collected on a filter, carefully edulcorated, heated to redness, and weighed.

To the clear liquid, containing peroxide of iron and alumina, a solution of pure potash is added in moderate excess; so as not only to throw down those oxides, but to redissolve the alumina. The peroxide of iron is then collected on a filter, edulcorated carefully until the washings cease to have an alkaline reaction, and is well dried and ignited, as described at page 1226. This operation, however, should be done with care; since any adhering particles of paper, or other combustible matter, would bring the iron into the state of black oxide, a change which is known to have occurred by the iron being attracted by a magnet.

To procure the alumina, the liquid in which it is dissolved is boiled with hydrochlorate of ammonia, when chloride of potassium is formed, the volatile alkali is dissipated in vapour, and the alumina subsides. As soon as the solution is thus rendered neutral, the hydrous alumina is collected on a filter, dried by exposure to a white heat, and quickly weighed after removal from the fire.

Separation of Iron and Manganese.—A compound of these metals or their oxides may be dissolved in hydrochloric acid. If the iron is in a large proportion compared with the manganese, the following process may be adopted with advantage:—To the cold solution, considerably diluted with water, and acidulated with hydrochloric acid, carbonate of soda is gradually added, and the liquid is briskly stirred with a glass rod during the effervescence, in order that it may become highly charged with carbonic acid. By neutralizing the solution in this manner, it at length attains a point at which the peroxide of iron is entirely deposited, leaving the liquid colourless; while the manganese, by aid of the free carbonic acid, is kept in solution. The iron, after subsiding, is collected on a filter, and its quantity determined in the usual manner. The filtered liquor is then boiled with an excess of carbonate of soda; and the precipitated carbonate of manganese is collected, heated to full redness in an open crucible, by which it is converted into the red oxide, and weighed. This method is one of some delicacy; but in skilful hands it affords a very accurate result. It may also be employed for separating iron from magnesia and lime as well as from manganese.

But if the proportion of iron is small compared with that of manganese, the best mode of separating it is by succinate of ammonia or soda, prepared by neutralizing a solution of succinic acid with either of those alkalies. That this process should succeed, it is necessary that the iron be wholly in the state of peroxide, that the solution be exactly neutral, which may easily be insured by the cautious use of ammonia, and that the reddish-brown coloured succinate of peroxide of iron be washed with cold water. When the precipitate is washed clean, solution of ammonia should be poured on it to separate succinic acid, and the remaining peroxide of iron may be dried, cautiously ignited, and weighed. From the filtered liquid the manganese may be precipitated at a boiling temperature by carbonate of soda, and its quantity determined in the way above mentioned. The benzoate may be substituted for succinate of ammonia in the preceding process.

It may be stated is a general rule, that, whenever it is intended to precipitate iron by means of the alkalies, the succinates, or benzoates, it is essential that this metal be in the maximum of oxidation. It is easily brought into this state by digestion with a little nitric acid.

Separation of Manganese from Lime and Magnesia.—If the quantity of the former is proportionally small, it is precipitated as a sulphuret by hydrosulphuret of ammonia or sulphuret of potassium. The sulphuret is then dissolved in hydrochloric acid, and the manganese thrown down as usual by means of an alkali. But if the manganese is the chief ingredient, the best method is to precipitate it at once, together with the two earths, by a fixed alkaline carbonate at a boiling temperature. The precipitate, after being exposed to a low red heat and weighed, is put into cold water acidulated with a drop or two of nitric acid, when the lime and magnesia will be slowly dissolved with effervescence. Should a trace of the manganese be likewise taken up, it may easily be thrown down by hydrosulphuret of ammonia.

Stromeyer has recommended a very elegant and still better process for removing small quantities of manganese from lime and magnesia. The solution is acidulated with nitric or hydrochloric acid; bicarbonate of soda is gradually added in very slight excess, stirring after each addition, that the liquid may be charged with carbonic acid; and a solution of chlorine, or a current of the gas, is introduced. The protoxide of manganese is converted by the chlorine into the insoluble hydrated peroxide, while any traces of lime or magnesia, which might otherwise fall, are retained in solution by means of carbonic acid. A solution of chloride of soda or lime is in fact our most delicate test for small quantities of manganese.

Mode of analyzing an Earthy Mineral containing Silica, Iron, Alumina, Manganese, Lime, and Magnesia.—The mineral, reduced to fine powder, is ignited with three or four times its weight of carbonate of potassa or soda, the mass is taken up in dilute hydrochloric acid, and the silica separated in the way already described. To the solution, thus freed from silica and duly acidulated, carbonate of soda, or still better the bicarbonate, is gradually added, so as to charge the liquid with carbonic acid, as in the analysis of iron and manganese. In this manner the iron and alumina are alone precipitated, substances which may be separated from each other by means of pure potassa (page 1235). The manganese, lime, and magnesia, may then be determined by the processes above described.

SECTION IV.

ANALYSIS OF MINERAL WATERS.

Rain water collected in clean vessels in the country, or freshly fallen snow when melted, affords the purest kind of water which can be procured without having recourse to distillation. The water obtained from these sources, however, is not absolutely pure, but contains a portion of carbonic acid and air, absorbed from the atmosphere. It is remarkable that this air is very rich in oxygen. That procured from snow water by boiling was found by Gay-Lussac and Humboldt to contain 34·8, and that from rain water 32 per cent. of oxygen gas. From the powerfully solvent properties of water, this fluid no sooner reaches the ground and percolates through the soil, than it dissolves some of the substances which it meets with in its passage. Under common circumstances it takes up so small a quantity of foreign matter, that its sensible properties are not materially affected, and in this state it gives rise to *spring*, *well*, and *river* water. Sometimes, on the contrary, it becomes so strongly impregnated with saline and other substances, that it acquires a peculiar flavour, and is thus rendered unfit for domestic uses. It is then known by the name of *mineral water*.

The composition of spring water is dependent on the nature of the soil through which it flows. If it has filtered through primitive strata, such as quartz rock, granite, and the like, it is in general very pure; but, if it meets with limestone or gypsum in its passage, a portion of these salts is dissolved, and communicates the property called *hardness*. Hard water is characterized by decomposing soap, the lime of the former yielding insoluble compounds with the margaric and oleic acids of the latter. If this defect is owing to the presence of carbonate of lime, it is easily remedied by boiling, when free carbonic acid is expelled, and the insoluble carbonate of lime subsides. If sulphate of lime is present, the addition of a little carbonate of soda, by precipitating the lime, converts the hard into soft water. Besides these ingredients, the chlorides of calcium and sodium are frequently contained in spring water.

Spring water, in consequence of its saline impregnation, is frequently unfit for chemical purposes, and on these occasions distilled water is employed. Distillation may be performed on a small scale by means of a retort, in the body of which water is made to boil, while the condensed vapour is received in a glass flask, called a *recipient*, which is adapted to its beak or open extremity. This process is more conveniently conducted, however, by means of a still.

The different kinds of mineral water may be conveniently arranged for the purpose of description in the six divisions of acidulous, alkaline, chalybeate, sulphureous, saline, and siliceous springs.

1. Acidulous springs, of which those of Seltzer, Spa, Pyrmont, and Carlsbad are the most celebrated, commonly owe their acidity to the presence of free carbonic acid, in consequence of the escape of which they sparkle when poured from one vessel into another. Such carbonated waters communicate a red tint to litmus paper before, but not after being boiled, and the redness disappears on exposure to the air. Mixed with a sufficient quantity of lime-

water, they become turbid from the deposition of carbonate of lime. They frequently contains carbonate of lime, magnesia, and protoxide of iron, in consequence of the facility with which these salts are dissolved by water charged with carbonic acid.

2. Alkaline waters are such as contain a free or carbonated alkali, and consequently, either in their natural state, or when concentrated by evaporation, possess an alkaline reaction.

These springs are rare. The best instance I have met with is in water collected at the Furnas, St. Michael's, Azores, and sent to the Royal Society of Edinburgh by Lord Napier. These springs contain carbonate of soda and carbonic acid, and are almost entirely free from earthy substances. Of five different kinds of these waters which I examined, the greater part also contained protoxide of iron, hydrosulphuric acid, and chloride of sodium.

3. Chalybeate waters are characterized by a strong styptic inky taste, and by striking a black colour with the infusion of gall-nuts. The iron is sometimes combined with hydrochloric or sulphuric acid; but most frequently it is in the form of protocarbonate, held in solution by free carbonic acid. On exposure to the air, the protoxide is oxidized, and the hydrated peroxide subsides, causing the ochreous deposit so commonly observed in the vicinity of chalybeate springs.

To ascertain the quantity of iron contained in a mineral water, a known weight of it is concentrated by evaporation, and the iron is brought to the state of peroxide by means of nitric acid. The peroxide is then precipitated by ammonia and weighed; and, if lime and magnesia are present, it may be separated from those earths by the process described in the last section.

Chalybeate waters are by no means uncommon; but the most noted in Britain are those of Tunbridge, Cheltenham, and Brighton. The Bath water also contains a small quantity of iron.

4. Sulphureous waters, of which the springs of Aix-la-Chapelle, Harrowgate, and Moffat afford examples, contain hydrosulphuric acid, and are easily recognised by their odour, and by causing a brown precipitate with a salt of lead or silver. The gas is readily expelled by boiling, and its quantity may be roughly estimated by transmitting it through a solution of pure chloride of mercury, and weighing the sulphuret which is generated.

5. Those mineral springs are called saline, the character of which is caused by saline compounds. The salts which are most

frequently contained in these waters are the sulphates and carbonates of lime, magnesia, and soda, and the chlorides of calcium, magnesium, and sodium. Potassa sometimes exists in them, and Berzelius has found lithia in the spring of Carlsbad. It has lately been discovered, that the presence of hydriodic acid in small quantity is not unfrequent. As examples of saline water may be enumerated the springs of Epsom, Cheltenham, Bath, Bristol, Barèges, Buxton, Pitcaithly, and Toeplitz.

The first object in examining a saline spring is to determine the nature of its ingredients. Hydrochloric acid is detected by nitrate of oxide of silver, and sulphuric acid by chloride of barium ; and, if an alkaline carbonate be present, the precipitate occasioned by either of these tests will contain a carbonate of oxide of silver or baryta. The presence of lime and magnesia may be discovered, the former by oxalate of ammonia, and the latter by phosphate of ammonia. Potassa is known by the action of chloride of platinum (page 377). To detect soda, the water should be evaporated to dryness, the deliquescent salts removed by alcohol, and the matter insoluble in that menstruum taken up by a small quantity of water, and be allowed to crystallize by spontaneous evaporation. The salt of soda may then be recognised by the rich yellow colour which it communicates to flame (page 383). If the presence of hydriodic acid be suspected, the solution is brought to dryness, the soluble parts dissolved in two or three drachms of a cold solution of starch, and strong sulphuric acid gradually added (page 302).

Having thus ascertained the nature of the saline ingredients, their quantity may be determined by evaporating a pint of water to dryness, heating to low redness, and weighing the residue. In order to make an exact analysis, a given quantity of the mineral water is concentrated in an evaporating basin as far as can be done without causing either precipitation or crystallization, and the residual liquid is divided into two equal parts. From one portion the sulphuric and carbonic acids are thrown down by nitrate of baryta, and, after collecting the precipitate on a filter, the hydrochloric acid is precipitated by nitrate of oxide of silver. The mixed sulphate and carbonate is exposed to a low red heat, and weighed ; and the carbonate is then dissolved by dilute hydrochloric acid, and its quantity determined by weighing the sulphate. The chloride of silver, of which 143·42 parts correspond to 36·42 of hydrochloric acid, is fused in a platinum spoon or crucible, in order to render it quite free from moisture. To the other half of the concentrated mineral water, oxalate of ammonia is added for the purpose of precipitating the lime; and the magnesia is afterwards thrown down as the ammoniaco-phosphate, by means of ammonia and phosphoric acid. Having thus determined the weight of each of the fixed ingredients excepting the soda, the loss is of course the quantity of that alkali required.

The individual constituents of the water being known, it remains to determine the state in which they were originally combined. In a mineral water containing sulphuric and hydrochloric acids, lime, and soda, it is obvious that three cases are possible. The liquid may contain sulphate of lime and chloride of sodium, or chloride of calcium and sulphate of soda; or each acid may be distributed between both the bases. It was at one time supposed that the lime must be in combination with sulphuric acid, because the sulphate of that earth is left when the water is evaporated to dryness. This, however, by no means follows. In whatever state the lime may exist in the original spring, gypsum will be generated as soon as the concentration reaches that degree at which sulphate of lime cannot be held in solution. The late Dr. Murray, who treated this question with much sagacity, observes that some mineral waters, which contain the four principles above mentioned, possess higher medicinal virtues than can be justly ascribed to the presence of sulphate of lime. He advances the opinion, that alkaline bases are united in mineral waters with those acids with which they form the most soluble compounds, and that the insoluble salts obtained by evaporation are merely products. He therefore proposes to arrange the substances determined by analysis according to this supposition. (Edin. Phil. Trans. vii.) To this practice there is no objection; but it is probable that each acid is rather distributed between several bases than combined exclusively with either.

Sea water may be regarded as one of the saline mineral waters. Its taste is disagreeably bitter and saline, and its fixed constituents amount to about three per cent. Its specific gravity varies from 1·0269 to 1·0285; and it freezes at about 28·5° F. A very complete analysis of the water of the English Channel was executed a few years ago by Dr. Schweitzer of Brighton, the results of which are subjoined:

	Grains.
Water	964·74372
Chloride of sodium	27·05948
Chloride of potassium	0·76552
Chloride of magnesium	3·66658
Bromide of magnesium	0·02929
Sulphate of magnesia	2·29578
Sulphate of lime	1·40662
Carbonate of lime	0·03301
	1000·00000

The water of the Dead Sea has a far stronger saline impregnation than sea water, containing one-fourth of its weight of solid matter. It has a peculiarly bitter, saline, and pungent taste, and its specific gravity is 1·211. According to the analysis of Marcet, 100 parts of it are composed of—muriate of magnesia 10·246, muriate of soda 10·36, muriate of lime 3·92, and sulphate of lime 0·054. In the river Jordan, which flows into the Dead Sea, Marcet discovered the same principles as in the lake itself.

6. Siliceous waters are very rare, and in those hitherto discovered the silica appears to have been dissolved by means of soda. The most remarkable of these are the boiling springs of the Geyser and Rykum in Iceland, a gallon of which, according to the analysis of Black, contains the following substances: (Edinburgh Philos. Trans. iii. 95 :)

	Geyser.	Rykum.
Soda	5·56	3·0
Alumina	2·80	0·29
Silica	31·50	21·83
Muriate of Soda	14·42	16·96
Sulphate of Soda	8·57	7·53

The hot springs of Pinnarkoon and Loorgootha in India are analogous to the foregoing. A gallon of the water yields about 24 grains of solid matter; and the saline contents, sent to Dr. Brewster by Mr. P. Breton, were found to consist of 21·5 per cent. of silica, 19 of chloride of sodium, 19 of sulphate of soda, 19 of carbonate of soda, pure soda 5, and 15·5 of water. (Edinburgh Journal of Science, No. xvii. p. 97.)

It is remarkable that nitrogen gas very generally occurs in hot springs. It was found by Longchamp in various hot springs of France, and a similar observation has been made by Dr. Daubeny. Its source is clearly referable to atmospheric air contained in water, which air has been deprived of its oxygen by chemical changes in the interior of the earth.

TABLE

Showing the Composition of several of the principal Mineral Waters. (From Dr. Henry's Elements.)

[N.B. The temperature, when not expressed, is to be understood to be 49° or 50° Fahrenheit.]

I. Carbonated Waters.

Seltzer. Bergmann.

In each wine pint.

Carbonic acid	17 cub. in.

Specific gravity 1·0027.

Carbonate of soda	4 grs.
——— of magnesia	5
——— of lime	3
Chloride of sodium	17
	29

Carlsbad. (Temperature 165° Fahr.) Berzelius.

In a wine pint.

Carbonic acid	5 cub. in.

In 1000 parts by weight.

Sulphate of soda . . .	2·58714 grs.
Carbonate of soda . .	1·25200
Chloride of sodium . .	1·04893
Carbonate of lime . .	0·31219
Fluoride of calcium . .	0·00331
Phosphate of lime . .	0·00019
Carbonate of strontia .	0·00097
——— of magnesia .	0·18221
Phosphate of alumina .	0·00034
Carbonate of iron . .	0·00424
——— of manganese,	a trace.
Silica	0·07504
	5·46656

Spa. Bergmann.

Specific gravity 1·0010.

In each wine pint.

Carbonic acid	13 cub. in.

Carbonate of soda	1·5 gr.
——— of magnesia . .	4·5
——— of lime	1·5
Chloride of sodium	0·2
Oxide of iron	0·6
	8·3

Pyrmont. Bergmann.

Specific gravity 1·0024.

In each wine pint.

Carbonic acid	26 cub. in.

Carbonate of magnesia . .	10· grs.
——— of lime	4·5
Sulphate of magnesia . .	5·5
——— of lime	8·5
Chloride of sodium	1·5
Oxide of iron	0·6
	30·6

Pouges. Hassenfratz.

In each wine pint.

Carbonic acid	30 cub. in.

Carbonate of soda	10· grs.
——— of magnesia . .	1·2
——— of lime	12·
Chloride of sodium	2·2
Oxide of iron	2·5
Silica	0·5
	28·4

Composition of Mineral Waters,—Continued.

II. SULPHURETTED WATERS.

AIX-LA-CHAPELLE. Bergmann.

Temperature 143°.

In each wine pint.

Sulphuretted hydrogen	5·5 cub. in.
Carbonate of soda	12· grs.
——— of lime	4·75
Muriate of soda	5·
	21·75

CHELTENHAM, Sulphur Spring.

Brande and Parkes.

Specific gravity 1·0085.

In each wine pint.

Carbonic acid	1·5 cub. in.
Sulphuretted hydrogen	2·5
Sulphate of soda	23·5 grs.
——— of magnesia	5·
——— of lime	1·2
Muriate of soda	35·
Oxide of iron	0·3
	65·

LEAMINGTON, Sulphur Water.

Scudamore.

Specific gravity 1·0042.

Sulphuretted hydrogen, quantity not ascertained.

In each pint.

Muriate of soda	15· grs.
——— of lime	7·96
——— of magnesia	3·30
Sulphate of soda	11·60
Oxide of iron	a trace.
	37·86

MOFFAT. Garnet.

Nitrogen	0·5 cub. in.
Carbonic acid	0·6
Sulphuretted hydrogen	1·2
Muriate of soda	4·5 grs.

HARROWGATE WATER.

New Well at the Crown Inn.

(West, Quart. Journ. xv. 82.)

Specific gravity 1·01286 at 69°.

One wine gallon contains

Sulphuretted hydrogen	6·4 cub. in.
Carbonic acid	5·25
Azote	6·5
Carburetted hydrogen	4·65
	22·8

Also,

Muriate of soda	735· grs.
——— of lime	71·5
——— of magnesia	43·
Bi-carbonate of soda	14·75
	864·25

Old Well.

Sp. gr. 1·01324 at 60°.

Sulphuretted hydrogen	14·0 cub. in.
Carbonic acid	4·25
Azotic gas	8·
Carburetted hydrogen	4·15
	30·4

Also,

Muriate of soda	752·0 grs.
——— of lime	65·75
——— of magnesia	29·2
Bi-carbonate of soda	12·8
	859·75

III. SALINE WATERS.

SEIDLITZ. Bergmann.

Specific gravity 1·0060.

In a pint.

Carbonate of magnesia	2·5
——— of lime	0·8
Sulphate of magnesia	180·
——— of lime	5·
Muriate of magnesia	4·5
	192·8

CHELTENHAM, pure Saline. Parkes and Brande.

In each pint.

Sulphate of soda	15·
——— of magnesia	11·
——— of lime	4·5
Muriate of soda	50·
	80·5

Composition of Mineral Waters,—Continued.

LEAMINGTON, Saline. Scudamore.

Specific gravity 1·0119.

In a pint.

Muriate of soda	53·75
——— of lime	28·64
——— of magnesia	20·16
Sulphate of soda	7·83
Oxide of iron	a trace.
	110·38

LEAMINGTON, Lord Aylesford's Spring. Scudamore.

Specific gravity 1·0093.

In a pint.

Muriate of soda	12·25
——— of lime	28·24
——— of magnesia	5·22
Sulphate of soda	32·96
Oxide of iron	a trace.
	78·67

BRISTOL. Carrick.

Temp. 74°. Specific gravity 1·00077.

In each pint.

Carbonic acid	3·5 cub. in.

Carbonate of lime	1·5 grs.
Sulphate of soda	1·5
——— of lime	1·5
Muriate of soda	0·5
——— of magnesia	1·
	6·0

BATH. Phillips.

Temp. 109° to 117°. Sp. gr. 1·002.

In each pint.

Carbonic acid	1·2 cub. in.

Carbonate of lime	0·8
Sulphate of soda	1·4
——— of lime	9·3
Muriate of soda	3·4
Silica	0·2
Oxide of iron	a trace.
	15·1

BATH. Solid contents. Scudamore.

Muriate of lime	1·2 grs.
——— of magnesia	1·6
Sulphate of lime	9·5
——— of soda	·9
Silica	·2
Oxide of iron	·01985
Loss, partly carb. of soda	·58015
	14·

Mr. Cuff has found both potash and iodine in the Bath waters.

BUXTON. Scudamore.

Sp. gr. at 60°, 1·0006. Temp. 82°.

In a wine gallon.

Carbonic acid	1·5 cub. in.
Nitrogen	4·64

Muriate of magnesia	·58 grs.
——— of soda	2·40
Sulphate of lime	·6
Carbonate of lime	10·40
Extractive and vegetable matter	0·50
Loss	0·52
	15·

Or, according to Dr. Murray's views.

Sulphate of soda	0·63
Muriate of lime	0·57
——— of soda	1·80
——— of magnesia	0·58
Carbonate of lime	10·40
Extract and loss	1·02
	15·00

MATLOCK BATH. Scudamore.

Temp. 68°. Sp. gr. 1·0003.

Free carbonic acid.

Muriates and sulphates of } magnesia, lime, and soda? in very minute quantities not yet ascertained.

Composition of Mineral Waters,—Continued.

IV. CHALYBEATE WATERS.

TUNBRIDGE. Scudamore.

Specific gravity 1·0007.

In each gallon.

Muriate of soda	2·46
——— of lime	0·39
——— of magnesia	0·29
Sulphate of lime	1·41
Carbonate of lime	0·27
Oxide of iron	2·22
Traces of manganese, vegetable fibre, silica, &c.	0·44
Loss	0·13
	7·61

CHELTENHAM. Brande and Parkes.

Specific gravity 1·0092.

In a pint.

Carbonic acid . . . 2·5 cub. in.

Carbonate of soda	0·5
Sulphate of soda	22·7
——— of magnesia	6·
——— of lime	2·5
Muriate of soda	41·3
Oxide of iron	0·8
	73·8

BRIGHTON. Marcet.

Specific gravity 1·00108.

Carbonic acid gas . . 2½ cub. in.

Sulphate of iron	1·80 grs.
——— of lime	4·09
Muriate of soda	1·53
——— of magnesia	0·75
Silica	0·14
Loss	0·19
	8·50

HARROWGATE, Oddie's Chalybeate.

Scudamore.

Specific gravity 1·0053.

In each gallon.

Muriate of soda	300·4
——— of lime	22·
——— of magnesia	9·9
Sulphate of lime	1·86
Carbonate of do.	6·7
——— of magnesia	0·8
Oxide of iron	2·40
Residue, chiefly silica	·40
	344·46

APPENDIX.

TABLE I.

Table of Chemical Equivalents of Elementary Substances.

Elements.	Equiv^{t}.	Elements.	Equiv^{t}.	Elements.	Equiv^{t}.
Aluminium	13·7	Gold	199·2	Potassium	39·15
Antimony	64·6	Hydrogen	1	Rhodium	52.2
Arsenic	37·7	Iodine	126·3	Selenium	39·6
Barium	68·7	Iridium	98·8	Silicium	22·5
Bismuth	71	Iron	28	Silver	108
Boron	10·9	Lead	103·6	Sodium	23·3
Bromine	78·4	Lithium	6	Strontium	43·8
Cadmium	55·8	Magnesium	12·7	Sulphur	16·1
Calcium	20·5	Manganese	27·7	Tellurium	64·2
Carbon	6·12	Mercury	202.	Thorium	59·6
Cerium	46	Molybdenum	47·7	Tin	57·9
Chlorine	35·42	Nickel	29·5	Titanium	24·3
Chromium	28	Nitrogen	14·15	Tungsten	99·7
Cobalt	29·5	Osmium	99·7	Vanadium	68·5
Columbium	185	Oxygen	8	Uranium	217
Copper	31·6	Palladium	53·3	Yttrium	32·2
Fluorine	18·68	Phosphorus	15·7	Zinc	32·3
Glucinium	26·5	Platinum	98·8	Zirconium	33·7

II.—*TABLE of the elastic Force of Aqueous Vapour at different Temperatures, expressed in Inches of Mercury.*

Temp.	Force of Vapour.		Temp.	Force of Vapour.		Temp.	Force of Vapour.	
	Dalton.	Ure.		Dalton.	Ure.		Dalton.	Ure.
32°F.	0·200	0·200	79°F.	0·971		126°F.	3·89	
33	0·207		80	1·00	1·010	127	4·00	
34	0·214		81	1·04		128	4·11	
35	0·221		82	1·07		129	4·22	
36	0·229		83	1·10		130	4·34	4·366
37	0·237		84	1·14		131	4·47	
38	0·245		85	1·17	1·170	132	4·60	
39	0·254		86	1·21		133	4·73	
40	0·263	0·250	87	1·24		134	4·86	
41	0·273		88	1·28		135	5·00	5·070
42	0·283		89	1·32		136	5·14	
43	0·294		90	1·36	1·360	137	5·29	
44	0·305		91	1·40		138	5·44	
45	0·316		92	1·44		139	5·59	
46	0·328		93	1·48		140	5·74	5·770
47	0·339		94	1·53		141	5·90	
48	0·351		95	1·58	1·640	142	6·05	
49	0·363		96	1·63		143	6·21	
50	0·375	0·360	97	1·68		144	6·37	
51	0·388		98	1·74		145	6·53	6·600
52	0·401		99	1·80		146	6·70	
53	0·415		100	1·86	1·860	147	6·87	
54	0·429		101	1·92		148	7·05	
55	0·443	0·416	103	1·98		149	7·23	
56	0·458		102	2·04		150	7·42	7·530
57	0·474		104	2·11		151	7·61	
58	0·490		105	2·18	2·100	152	7·81	
59	0·507		106	2·25		153	8·01	
60	0·524	0·516	107	2·32		154	8·20	
61	0·542		108	2·39		155	8·40	8·500
62	0·560		109	2·46		156	8·60	
63	0·578		110	2·53	2·456	157	8·81	
64	0·597		111	2·60		158	9·02	
65	0·616	0·630	112	2·68		159	9·24	
66	0·635		113	2·76		160	9·46	9·600
67	0·655		114	2·84		161	9·68	
68	0·676		115	2·92	3·820	162	9·91	
69	0·698		116	3·00		163	10·15	
70	0·721	0·726	117	3·08		164	10·41	
71	0·745		118	3·16		165	10·68	10·800
72	0·770		119	3·25		166	10·96	
73	0·796		120	3·33	2·300	167	11·25	
74	0·823		121	3·42		168	11·54	
75	0·851	0·860	122	3·50		169	11·83	
76	0·880		123	3·59		170	12·13	12·050
77	0·910		124	3·69		171	12·43	
78	0·940		125	3·79	3·830	172	12·73	

Temp.	Force of Vapour.	
	Dalton.	Ure.
173°F.	13·02	
174	13·32	
175	13·62	13·550
176	13·92	
177	14·22	
178	14·52	
179	14·83	
180	15·15	15·160
181	15·50	
182	15·86	
183	16·23	
184	16·61	
185	17·00	16·900
186	17·40	
187	17·80	
188	18·20	
189	18·60	
190	19·00	19·000
191	19·42	
192	19·86	
193	20·32	
194	20·77	
195	21·22	21·100
196	21·68	
197	22·13	
198	22·69	
199	23·16	
200	23·64	23·600
201	24·12	
202	24·61	
203	25·10	
204	25·61	
205	26·13	25·900
206	26·66	
207	27·20	
208	27·74	
209	28·29	
210	28·84	28·880
211	29·41	
212	30·00	30·000
213	30·60	
214	31·21	
215	31 83	
216	32·46	33·400
217	33·09	
218	33·72	
219	34·35	
220	34·99	35·540
221	35·63	36·700
222	36·25	
223	36·88	
224°F.	37·53	
225	38·20	39·110
226	38·89	40·100
227	39·59	
228	40·30	
229	41·02	
230	41·75	43·100
231	42·49	
232	43·24	
233	44·00	
234	44·78	46·800
235	45·58	47·220
236	46·39	
237	47·20	
238	48·02	50·300
239	48 84	
240	49·67	51·700
241	50·50	
242	51·34	53·600
243	52·18	
244	53·03	
245	53·88	56·340
246	54·68	
247	55·54	
248	56·42	60·400
249	57·31	
250	58·21	61·900
251	59·12	63·500
252	60 05	
253	61·00	
254	61·92	66·700
255	62·85	67·250
256	63·76	
257	64·82	69·800
258	65·78	
259	66·75	
260	67·73	72·300
261	68·72	
262	69·72	75·900
263	70·73	
264	71·74	77·900
265	72·76	78·040
266	73·77	
267	74·79	81·900
268	75·80	
269	76·82	84·900
270	77·85	86·300
271	78·89	88·000
272	79·94	
273	80·98	91·200
274	82 01	
275°F.	83·13	93·480
276	84·35	
277	85·47	97·800
278	86·50	
279	87·63	101·600
280	88·75	101·900
281	89·87	104·400
282	90·99	
283	92·11	107·700
284	93·23	
285	94·35	112·200
286	95·48	
287	96·64	114·800
288	97·80	
289	98·96	118·200
290	100·12	120·150
291	101·28	
292	102·45	123·100
293	103·63	
294	104·80	126·700
295	105·97	129·000
296	107·14	
297	108·31	133·900
298	109·48	137·400
299	110·64	
300	111·81	139·700
301	112·98	
302	114·15	144·300
303	115·32	147·700
304	116·50	
305	117·68	150·560
306	118·86	154·400
307	120·03	
308	121·20	157·700
309	122·37	
310	123·53	161·300
311	124·69	164·800
312	125·85	167·000
313	127·00	
314	128·15	
315	129·29	
316	130·43	
317	131·57	
318	132·72	
319	133·86	
320	135·00	
321	136·14	
322	137·28	
323	138·42	
324	139·56	
325	140·70	

TABLE III.

Dr. Ure's Table, showing the elastic Force of the Vapours of Alcohol, Ether, Oil of Turpentine, and Petroleum or Naphtha, at different Temperatures, expressed in Inches of Mercury.

Ether.		Alcohol sp. gr. 0·813.		Alcohol sp. gr. 0·813.		Petroleum.	
Temp.	Force of Vapour.	Temp.	Force of Vapour.	Temp.	Force of Vapour.	Temp.	Force of Vapour.
34°	6·20	32°	0·40	193·3°	46·60	316°	30·00
44	8·10	40	0·56	196·3	50·10	320	31·70
54	10·30	45	0·70	200	53·00	325	34·00
64	10·00	50	0·86	206	60·10	330	36·40
74	16·10	55	1·00	210	65·00	335	38·90
84	20·00	60	1·23	214	69·30	340	41·60
94	24·70	65	1·49	216	72·20	345	44·10
104	30·00	70	1·76	220	78·50	350	46·86
105	30·00	75	2·10	225	87·50	355	50·20
110	32·54	80	2·45	230	94·10	360	53·30
115	35·90	85	2·93	232	97·10	365	56·90
120	39·47	90	3·40	236	103·60	370	60·70
125	43·24	95	3·90	238	106·90	372	61·90
130	47·14	100	4·50	240	111·24	375	64·00
135	51·90	105	5·20	244	118·20		
140	56·90	110	6·00	247	122·10	Oil of Turpentine.	
145	62·10	115	7·10	248	126·10		
150	67·60	120	8·10	249·7	131·40	Temp.	Force of Vapour.
155	73·60	125	9·25	250	132·30		
160	80·30	130	10·60	252	138·60	304°	30·00
165	86·40	135	12·15	254·3	143·70	307·6	32·60
170	92·80	140	13·90	258·6	151·60	310	33·50
175	99·10	145	15·95	260	155·20	315	35·20
180	108·30	150	18·00	262	161·40	320	37·06
185	116·10	155	20·30	264	166·10	322	37·80
190	124·80	160	22·60			326	40·20
195	133·70	165	25·40			330	42·10
200	142·80	170	28·30			336	45·00
205	151·30	173	30·00			340	47·30
210	166·00	178·3	33·50			343	49·40
		180	34·73			347	51·70
		182·3	36·40			350	53·80
		185·3	39·90			354	56·60
		190	43·20			357	58·70
						360	60·80
						362	62·40

TABLE IV.

For the conversion of Degrees on the Centigrade Thermometer into Degrees of Fahrenheit's Scale.

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
—50°	—58°.0	—6°	21°.2	38°	100°.4	82°	179°.6
—49	—56.2	—5	23.0	39	102.2	83	181.4
—48	—54.4	—4	24.8	40	104.0	84	183.2
—47	—52.6	—3	26.6	41	105.8	85	185.0
—46	—50.8	—2	28.4	42	107.6	86	186.8
—45	—49.0	—1	30.2	43	109.4	87	188.6
—44	—47.2	0	32.0	44	111.2	88	190.4
—43	—45.4	+1	33.8	45	113.0	89	192.2
—42	—43.6	2	35.6	46	114.8	90	194.0
—41	—41.8	3	37.4	47	116.6	91	195.8
—40	—40.0	4	39.2	48	118.4	92	197.6
—39	—38.2	5	41.0	49	120.2	93	199.4
—38	—36.4	6	42.8	50	122.0	94	201.2
—37	—34.6	7	44.6	51	123.8	95	203.0
—36	—32.8	8	46.4	52	125.6	96	204.8
—35	—30.0	9	48.2	53	127.4	97	206.6
—34	—29.2	10	50.0	54	129.2	98	208.4
—33	—27.4	11	51.8	55	131.0	99	210.2
—32	—25.6	12	53.6	56	132.8	100	212.0
—31	—23.8	13	55.4	57	134.6	101	213.8
—30	—22.0	14	57.2	58	136.4	102	215.6
—29	—20.2	15	59.0	59	138.2	103	217.4
—28	—18.4	16	60.8	60	140.0	104	219.2
—27	—16.6	17	62.6	61	141.8	105	221.0
—26	—14.8	18	64.4	62	143.6	106	222.8
—25	—13.0	19	66.2	63	145.4	107	224.6
—24	—11.2	20	68.0	64	147.2	108	226.4
—23	—9.4	21	69.8	65	149.0	109	228.2
—22	—7.6	22	71.6	66	150.8	110	230.0
—21	—5.8	23	73.4	67	152.6	111	231.8
—20	—4.0	24	75.2	68	154.4	112	233.6
—19	—2.2	25	77.0	69	156.2	113	235.4
—18	—0.4	26	78.8	70	158.0	114	237.2
—17	+1.4	27	80.6	71	159.8	115	239.0
—16	3.2	28	82.4	72	161.6	116	240.8
—15	5.0	29	84.2	73	163.4	117	242.6
—14	6.8	30	86.0	74	165.2	118	244.4
—13	8.6	31	87.8	75	167.0	119	246.2
—12	10.4	32	89.6	76	168.8	120	248.0
—11	12.2	33	91.4	77	170.6	121	249.8
—10	14.0	34	93.2	78	172.4	122	251.6
—9	15.8	35	95.0	79	174.2	123	253.4
—8	17.6	36	96.8	80	176.0	124	255.2
—7	19.4	37	98.6	81	177.8	125	257.0

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
126°	258°.8	175°	347°.0	224°	435°.2	273°	523°.4
127	260.6	176	348.8	225	437.0	274	525.2
128	262.4	177	350.6	226	438.8	275	527.0
129	264.2	178	352.4	227	440.6	276	528.8
130	266.0	179	354.2	228	442.4	277	530.6
131	267.8	180	356.0	229	444.2	278	532.4
132	269.6	181	357.8	230	446.0	279	534.2
133	271.4	182	359.6	231	447.8	280	536.0
134	273.2	183	361.4	232	449.6	281	537.8
135	275.0	184	363.2	233	451.4	282	539.6
136	276.8	185	365.0	234	453.2	283	541.4
137	278.6	186	366.8	235	455.0	284	543.2
138	280.4	187	368.6	236	456.8	285	545.0
139	282.2	188	370.4	237	458.6	286	546.8
140	284.0	189	372.2	238	460.4	287	548.6
141	285.8	190	374.0	239	462.2	288	550.4
142	287.6	191	375.8	240	464.0	289	552.2
143	289.4	192	377.6	241	465.8	290	554.0
144	291.2	193	379.4	242	467.6	291	555.8
145	293.0	194	381.2	243	469.4	292	557.6
146	294.8	195	383.0	244	471.2	293	559.4
147	296.6	196	384.8	245	473.0	294	561.2
148	298.4	197	386.6	246	474.8	295	563.0
149	300.2	198	388.4	247	476.6	296	564.8
150	302.0	199	390.2	248	478.4	297	566.6
151	303.8	200	392.0	249	480.2	298	568.4
152	305.6	201	393.8	250	482.0	299	570.2
153	307.4	202	395.6	251	483.8	300	572.0
154	309.2	203	397.4	252	485.6	301	573.8
155	311.0	204	399.2	253	487.4	302	575.6
156	312.8	205	401.0	254	489.2	303	577.4
157	314.6	206	402.8	255	491.0	304	579.2
158	316.4	207	404.6	256	492.8	305	581.0
159	318.2	208	406.4	257	494.6	306	582.8
160	320.0	209	408.2	258	496.4	307	584.6
161	321.8	210	410.0	259	498.2	308	586.4
162	323.6	211	411.8	260	500.0	309	588.2
163	325.4	212	413.6	261	501.8	310	590.0
164	327.2	213	415.4	262	503.6	311	591.8
165	329.0	214	417.2	263	505.4	312	593.6
166	330.8	215	419.0	264	507.2	313	595.4
167	332.6	216	420.8	265	509.0	314	597.2
168	334.4	217	422.6	266	510.8	315	599.0
169	336.2	218	424.4	267	512.6	316	600.8
170	338.0	219	426.2	268	514.4	317	602.6
171	339.8	220	428.0	269	516.2	318	604.4
172	341.6	221	429.8	270	518.0	319	606.2
173	343.4	222	431.6	271	519.8	320	608.0
174	345.2	223	433.4	272	521.6		

TABLE V.

Dr. Ure's Table of the Quantity of Oil of Vitriol, of sp. gr. 1·8485, *and of Anhydrous Acid, in* 100 *Parts of dilute Sulphuric Acid, at different Densities.*

Liquid.	Sp. Gr.	Dry.	Liquid.	Sp. Gr.	Dry.	Liquid.	Sp. Gr.	Dry.
100	1·8485	81·54	66	1·5503	53·82	32	1·2334	26·09
99	1·8475	80·72	65	1·5390	53·00	31	1·2260	25·28
98	1·8460	79·90	64	1·5280	52·18	30	1·2184	24·46
97	1·8439	79·09	63	1·5170	51·37	29	1·2108	23·65
96	1·8410	78·28	62	1·5066	50·55	28	1·2032	22·83
95	1·8376	77·46	61	1·4960	49·74	27	1·1956	22·01
94	1·8336	76·65	60	1·4860	48·92	26	1·1876	21·20
93	1·8290	75·83	59	1·4760	48·11	25	1·1792	20·38
92	1·8233	75·02	58	1·4660	47·29	24	1·1706	19·57
91	1·8179	74·20	57	1·4560	46·48	23	1·1626	18·75
90	1·8115	73·39	56	1·4460	45·66	22	1·1549	17·94
89	1·8043	72·57	55	1·4360	44·85	21	1·1480	17·12
88	1·7962	71·75	54	1·4265	44·03	20	1·1410	16·31
87	1·7870	70·94	53	1·4170	43·22	19	1·1330	15·49
86	1·7774	70·12	52	1·4073	42·40	18	1·1246	14·68
85	1·7673	69·31	51	1·3977	41·58	17	1·1165	13·86
84	1·7570	68·49	50	1·3884	40·77	16	1·1090	13·05
83	1·7465	67·68	49	1·3788	39·95	15	1·1019	12·23
82	1·7360	66·86	48	1·3697	39·14	14	1·0953	11·41
81	1·7245	66·05	47	1·3612	38·32	13	1·0887	10·60
80	1·7120	65·23	46	1·3530	37·51	12	1·0809	9·78
79	1·6993	64·42	45	1·3440	36·69	11	1·0743	8·97
78	1·6870	63·60	44	1·3345	35·88	10	1·0682	8·15
77	1·6750	62·78	43	1·3255	35·06	9	1·0614	7·34
76	1·6630	61·97	42	1·3165	34·25	8	1·0544	6·52
75	1·6520	61·15	41	1·3080	33·43	7	1·0477	5·71
74	1·6415	60·34	40	1·2999	32·61	6	1·0405	4·89
73	1·6321	59·52	39	1·2913	31·80	5	1·0336	4·08
72	1·6204	58·71	38	1·2826	30·98	4	1·0268	3·26
71	1·6090	57·89	37	1·2740	30·17	3	1·0206	2·446
70	1·5975	57·08	36	1·2654	29·35	2	1·0140	1·63
69	1·5868	56·26	35	1·2572	28·54	1	1·0074	0·8154
68	1·5760	55·45	34	1·2490	27·72			
67	1·5648	54·63	33	1·2409	26·91			

TABLE VI.

Dr. Ure's Table of the Quantity of Real or Anhydrous Nitric Acid in 100 *Parts of Liquid Acid, at different Densities.*

Specific Gravity.	Real acid in 100 parts of the Liquid.	Specific Gravity.	Real acid in 100 parts of the Liquid.	Specific Gravity.	Real acid in 100 parts of the Liquid
1·5000	79·700	1·3783	52·602	1·1895	26·301
1·4980	78·903	1·3732	51·805	1·1833	25·504
1·4960	78·106	1·3681	51·068	1·1770	24·707
1·4940	77·309	1·3630	50·211	1·1709	23·910
1·4910	76·512	1·3579	49·414	1·1648	23·113
1·4880	75·715	1·3529	48·617	1·1587	22·316
1·4850	74·918	1·3477	47·820	1·1526	21·519
1·4820	74·121	1·3427	47·023	1·1465	20·722
1·4790	73·324	1·3376	46·226	1·1403	19·925
1·4760	72·527	1·3323	45·429	1·1345	19·128
1·4730	71·730	1·3270	44·632	1·1286	18·331
1·4700	70·933	1·3216	43·835	1·1227	17·534
1·4670	70·136	1·3163	43·038	1·1168	16·737
1·4640	69·339	1·3110	42·241	1·1109	15·940
1·4600	68·542	1·3056	41·444	1·1051	15·143
1·4570	67·745	1·3001	40·647	1·0993	14·346
1·4530	66·948	1·2947	39·850	1·0935	13·549
1·4500	66·155	1·2887	39·053	1·0878	12·752
1·4460	65·354	1·2826	38·256	1·0821	11·955
1·4424	64·557	1·2765	37·459	1·0764	11·158
1·4385	63·760	1·2705	36·662	1·0708	10·361
1·4346	62·963	1·2644	35·865	1·0651	9·564
1·4306	62·166	1·2583	35·068	1·0595	8·767
1·4269	61·369	1·2523	34·271	1·0540	7·970
1·4228	60·572	1·2462	33·474	1·0485	7·173
1·4189	59·775	1·2402	32·677	1·0430	6·376
1·4147	58·978	1·2341	31·880	1·0375	5·579
1·4107	58·181	1·2277	31·083	1·0320	4·782
1·4065	57·384	1·2212	30·286	1·0267	3·985
1·4023	56·587	1·2148	29·489	1·0212	3·188
1·3978	55·790	1·2084	28·692	1·0159	2·391
1·3945	54·993	1·2019	27·895	1·0106	1·594
1·3882	54·196	1·1958	27·098	1·0053	0·797
1·3833	53·399				

VII.—*Table of Lowitz showing the Quantity of absolute Alcohol in Spirits of different Specific Gravities.*

100 Parts.		Sp. Gravity.		100 Parts.		Sp. Gravity.		100 Parts.		Sp. Gravity.	
Alc.	Wat.	At 68°.	At 60°.	Alc.	Wat.	At 68°.	At 60°.	Alc.	Wat.	At 68°.	At 60°.
100	0	0·791	0.796	66	34	0·877	0·881	32	68	0·952	0·955
99	1	0·794	0·798	65	35	0·880	0·883	31	69	0·954	0·957
98	2	0 797	0·801	64	36	0·882	0·886	30	70	0·956	0·958
97	3	0·800	0·804	63	37	0·885	0·889	29	71	0·957	0·960
96	4	0·803	0·807	62	38	0·887	0·891	28	72	0·959	0·962
95	5	0·805	0·809	61	39	0·889	0·893	27	73	0·961	0·963
94	6	0·808	0·812	60	40	0·892	0·896	26	74	0·963	0·965
93	7	0·811	0·815	59	41	0·894	0·898	25	75	0·965	0·967
92	8	0·813	0·817	58	42	0·896	0·900	24	76	0 966	0·968
91	9	0·816	0·820	57	43	0·899	0·902	23	77	0·968	0·970
90	10	0·818	0·822	56	44	0·901	0·904	22	78	0·970	0·972
89	11	0·821	0·825	55	45	0·903	0·906	21	79	0·971	0·973
88	12	0·823	0·827	54	46	0 905	0·908	20	80	0·973	0·974
87	13	0·826	0·830	53	47	0·907	0·910	19	81	0·974	0·975
86	14	0·828	0 832	52	48	0·909	0·912	18	82	0·976	0·977
85	15	0·831	0·835	51	49	0·912	0·915	17	83	0·977	0·978
84	16	0·834	0·838	50	50	0·914	0·917	16	84	0·978	0·979
83	17	0·836	0·840	49	51	0·917	0·920	15	85	0·980	0·981
82	18	0·839	0·843	48	52	0·919	0·922	14	86	0·981	0·982
81	19	0·842	0·846	47	53	0·921	0·924	13	87	0·983	0·984
80	20	0·844	0·848	46	54	0·923	0·926	12	88	0·985	0·986
79	21	0·847	0·851	45	55	0·925	0·928	11	89	0·986	0·987
78	22	0·849	0·853	44	56	0·927	0·930	10	90	0·987	0·988
77	23	0·851	0·855	43	57	0·930	0·933	9	91	0·988	0·989
76	24	0·853	0·857	42	58	0·932	0·935	8	92	0·989	0·990
75	25	0·856	0·860	41	59	0·934	0·937	7	93	0·991	0·991
74	26	0·859	0·863	40	60	0·936	0·939	6	94	0·992	0·992
73	27	0·861	0·865	39	61	0·938	0·941	5	95	0·994	
72	28	0·863	0·867	38	62	0·940	0·943	4	96	0·995	
71	29	0·866	0·870	37	63	0·942	0·945	3	97	0·997	
70	30	0·868	0·872	36	64	0·944	0·947	2	98	0·998	
69	31	0·870	0·874	35	65	0·946	0·949	1	99	0·999	
68	32	0 872	0·875	34	66	0 948	0·951	0	100	1·000	
67	33	0·875	0·879	33	67	0·950	0·953				

VIII.—*Tables showing the Specific Gravity of Liquids, at the Temperature of 55° Fahr. corresponding to the Degrees of Beaumé's Hydrometer.*

FOR LIQUIDS LIGHTER THAN WATER.

Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.
10=	1·000	17=	·949	23=	·909	29=	·874	35=	·842
11	·990	18	·942	24	·903	30	·867	36	·837
12	·985	19	·935	25	·897	31	·861	37	·832
13	·977	20	·928	26	·892	32	·856	38	·827
14	·970	21	·922	27	·886	33	·852	39	·822
15	·963	22	·915	28	·880	34	·847	40	·817
16	·955								

FOR LIQUIDS HEAVIER THAN WATER.

Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.
0=	1·000	15=	1·114	30=	1·261	45=	1·455	60=	1·717
3	1·020	18	1·140	33	1·295	48	1·500	63	1·779
6	1·040	21	1·170	36	1·333	51	1·547	66	1·848
9	1·064	24	1·200	39	1·373	54	1·594	69	1·920
12	1·089	27	1·230	42	1·414	57	1·659	72	2·000

INDEX.

A.

Absinthiine, 1119
Absolute alcohol, 828
Acetal, 870
Acetates, 879
    products of decomposition of, 900
Acetone, 900
    its compounds and products, 900
Acetic acid,
    hydrated, 879
    products of decomposition of, 900
Acetule, 868
    chloride of, 889
    combinations of, 985
Acids, definition of, 570
    nomenclature of, 136
    animal, 1038
Acid, acetic and acetous, 867, 874
    acetulous, 872
    acetylic, 874
    aconitic, 1006
    adipic, 1060
    allantoic, 761
    aldehydic, 826, 872
    aloeresinic, 1148
    aloetic, 1148
    althionic, 866
    alloxanic, 764
    ambreic, 1083
    amygdalinic, 803
    anilic, 1143
    anthranilic, 1144
    antimonic and antimonious, 497
    arsenic, 463
    arsenious, 456
    arseniovinic, 825
    aspartic, 1150
    auric, 540
    azomaric, 1107
    benzilic, 801
    benzoic, 781
    bibromisatic, 1139
    bichlorisatic, 1139
Acid, bichlorisatydic, 1140
    boletic, 1086
    boracic, 262
    boro-hydrofluoric, 1086
    brombenzoic, 792
    bromic, 313
    bromosaliculic, 814
    butyric, capric, and caproic, 1024
    caffeic, 1086
    caincic, 1085
    camphoric, 1027
    capric, 1025
    carbazotic, 1143
    carbonic, 235
    mode of obtaining in a solid state, 57
    low temperature of, in the solid state, 57
    caryophyllic, 1033
    cerebric, 1196
    cetulic, 1038
    chelidonic, 1085
    chloranilic, 1140
    chloric, 285
    chlorinized chlorindoptenic, 1141
    chlorindoptenic, 1141
    chlorisatic, 1139
    chlorisatydic, 1140
    chloroacetic, 892
    chlorocarbonic, 292, 704
    chloronaphthalosic, 1181
    chloroproteic, 1184
    chlorosaliculic, 813
    chlorous, 284
    chlorovalerasic, 1031
    chlorovalerisic, 1031
    choleic, 1200
    choloidic, 1200
    cholesteric, 1083
    cholic, 1201
    chromic, 471
    chrysanilic, 1144
    chrysammic, 1148
Acid, chrysolepic, 1149
    cinnamic, 821
    citraconic, 1008
    citric, 1002
    cocoic, 1034
    colopholic, 1107
    columbic, 491
    crameric, 1086
    crenic and apocrenic, 1177
    croconic, 707
    crotonic, 1027
    cuminic, 1033
    cyanic, 709
    cyanilic, 752
    cyanuric, 717
    cynoxalic, 760
    elaidic, 1057
    ellagic, 999
    equisetic, 1019
    erythroleic, 1133
    ethionic, 863
    ethero-phosphoric, 846
    ethero-sulphuric, 838
    ferrocyanic, 731
    fluoboric, 320
    fluochromic, 473
    fluoric, 319
    fluosilicic, 318, 322
    formic, 967
    formobenzoic, 778
    fulminic, 714
    fumaric, 1021
    fungic, 1086
    gallic, 995
    glacial phosphoric, 260
    glucic, 929
    hippuric, 789
    hircic, 1026
    hydrated saliculous, 809
    hydriodic, 301
    hydrobromic, 311
    hydrochloric, 276
    hydro-chloro-cyanic, 716

Acid, hydro-cobalto-cyanic, 741
hydrocyanic, 720
hydro-ferrid-cyanic, 739
hydroferrocyanic, 731
hydrofluoric, 317
hydroleic, 1071
hydromargaric, 1069
hydromargaritic, 1069
hydromellonic, 751
hydro-persulpho-cyanic, 753
hydropersulphuric, 333
hydroselenic, 338
hydrosulphocyanic, 746
hydrosulphuric, 758
hydrotelluric, 512
hypochlorous, 281
hyponitrous, 222
hypophosphomesitylous, 905
hypophosphorous, 255
hyposulphobenzidic, 794
hyposulphobenzoic, 791
hyposulphoindigotic, 1136
hyposulphuric, 250, 333
hyposulphurous, 249
indigotic, 1143
iodic, 303
iodosaliculic, 814
iodous, 303
isatic, 1137
isethionic, 863
itaconic, 1007
japonic, 1001
kakodylic, 910
kinic, 1022
komenic, 989
lactic, 949
lampic, 872
lipic, 1060
lithic, 759
lithofellic, 1202
maleic, 1021
malic, 1019
manganic, 420
margaric, 1038
margaritic, 1063
meconic, 989
mechloic, 1124
melangallic, 997
melanic, 812
melassic, 929
mellitic, 708
mesoxalic, 765
Acid, metagallic, 998
metamargaric, 1068
metameconic, 991
metaphosphoric, 257, 260
methionate of baryta, 866
methionic, 866
metoleic, 1071
molybdic and molybdous, 485
mucic, 937
muriatic, 276
mykomelinic, 766
nitric, 226
nitro-meconic, 1124
nitro-muriatic, 280
nitronaphthalic, 1182
nitro-picric, 1143
nitro-saliculic, 815
nitrous, 224
œnanthic, 1032
oleic, 1052
oleophosphoric, 1196
osmic, 555
oxalic, 698
oxalovinic, 853
oxaluric, 767
oxymuriatic, 271
palmic, 1074
palmitic, 1037
parabanic, 767
paraphosphoric, 257
paratartaric, 1008
perchloric, 286
periodic, 305
permanganic, 421
phocenic, 1026
phosphatic, 256
phosphomesitylic, 905
phosphoric, 257
phosphorous, 256
phosphovinic, 825
picric, 1143
pimaric, 1107
pimelic, 1060
pinic, 1107
polychromic, 1148
prussic, 720
pyrocitric, 1002
pyrogallic, 996, 997
pyroligneous, 877
pyromalic, 1019
pyromaric, 1107
pyromeconic, 992
pyromucic, 938, 940
pyrophosphoric, 257, 259
racemic, 1017
rhodizonic, 706
rocellic, 1032
rubinic, 1001
Acid, sabadillic, 1026
saccharic, 931
saccharosulphuric, 915
sacchulmic, 928
saliculous and saliculic, 809, 813
saponic, 1122
sebacic, 1056
selenic, 269
selenious, 268
silicic, 265
silico-fluoric, 322
sericic, 1035
stearic, 1040
suberic, 1048
succinic, 1049
sulphobenzidic, 794
sulphocyanic, 746
sulphoethulic, 836
sulphoindigotic, 1135
sulphomesitylic, 904
sulphonaphthalic, 1180
sulphoproteic, 1184
sulphopurpuric, 1136
sulphosaccharic, 926
sulphovinic, 825, 833
sulphur, 245
sulphuric, 245
fuming, 246
sulphurous, 244
sylvic, 1107
tannic, 993
tartaric, 1008
tartralic, 1016
telluric, 511
tellurous, 510
thionuric, 769
titanic, 508
tungstic, 488
uramilic, 771
uric, 759
valerianic, 985, 1030
vanadic, 480
veratric, 1033
of the Vosges, 1017
xanthic, 855
xanthoproteic, 1185
Acids, organic, 686
classification of, 691
a table of those for the detection of which directions are given in section on chemical analysis, 1230
theory of, 686
Acidulous waters, 1238
Aconitates, 1007
Aconitine, 1167
Acroleine, 1065

- Aëriform bodies, 28, 44
- Affinity, chemical, 139
  - table of, 140
  - single elective, 140
  - double elective, 143
  - disposing, 198
  - by what circumstances modified, 146
  - quiescent and divellent, 143
  - measure of, 154
  - changes that accompany, 143
- Agedoile, 1150
- Agriculture, chemistry of, 1211
  - of Liebig, 1222
- Air, atmospheric, 205
  - alkaline, 324
  - fixed, 235
- Alabaster, 604
- Albumen, 1185
  - identity of vegetable and animal, 1186
- Alcohol, 828
  - products of decomposition of, 895
  - acetification of, 874
  - and ammonia, 830
  - and iodine, 830
  - and salts, 831
- Aldehydammonia, 870
- Aldehydates, 872
- Aldehyde, 859, 869
  - products of decomposition of, 871
  - resin of, 871
- Alembroth, salt of, 667, 696
- Algaroth, powder of, 494
- Alizarine, 1116
- Alkalies, 369
  - metallic bases of, 371
  - volatile, 324
  - silicated, 266
  - vegetable, 1151
- Alkalimeter, 645
- Alkaline air, 324
  - bases, 567
- Alkaline earths, 369
  - metallic bases of, 388
- Alkaline waters, 1239
- Alkaloids, 1151
- Alkarsine, 907
- Allanite, 503
- Allantoine, 761
- Alloxan, 762
- Alloxanates, 765
- Alloxantine, 772
- Alloys, 558
  - of arsenic, 561
  - of tin, lead, antimony, and bismuth, 562
- Alloys, of copper, 553
  - of steel and silver, 564
  - of gold, 565
- Almond oil, 1080
- Aloes, bitter of, 1147, 1148
- Alpha orceine, 1133
- Altheine, 1150
- Althionates, 866
- Alum, 610
  - stone, 610
- Alumen ustum, 610
- Alumina, or aluminous earth, 403
  - tests of, 407
  - mellitate of, 709
  - benzoate, 783
  - sulphates of, 605
  - sulphates, double, of, 610
  - acetate of, 882
- Aluminite, 606
- Aluminium and its compounds, 401
- Amalgam, 558, 561
  - for looking-glasses, 561
  - ammoniacal, 694
  - for electrical machine, 561
- Amalgamation of silver ores, 533
- Amule, or amyle, 982
  - compounds of, 982
  - salts of, 984
  - products of, 985
- Amarythrine, 1130
- Amanitine, 1125
- Amber, 1083
- Ambergris and ambreine, 1083
- Amide, 328, 693
  - combinations of, 695
- Amilene, 985
- Ammelide, 756
- Ammeline, 755
  - and acids, 756
- Ammonia, 693
- Ammonia, liquid, table of the strength of solutions of, 328
  - character of the salts of, 326
  - cobaltate of, 450
  - sulphate of, 603
  - sulphates, double of, 613
  - sulphite of, 614
  - nitrate of, 618
  - phosphates of, 631
  - arseniates of, 458
- Ammonia, carbonates of, 648
  - hydrosalts of, 653
  - sulphur salts of, 657
  - haloid salts of, 667
  - chlorides with, 674
  - oxalate of, 701
  - acetate of, 880
  - lactate of, 951
  - magnesian phosphate of, 632
  - subcarbonate of, 648
  - bimalate of, 1019
  - citrate of, 1003
  - succinate of, 1050
  - urate of, 1205
  - mellitate of, 708
  - cyanates of, 710
  - cyanurate of, 718
  - hydrocyanate of, 724
  - oxalurate of, 768
  - thionurate of, 769
  - benzoate of, 782
  - saliculite of, 811
  - isethionate of, 865
  - table of salts of, 654
- Ammoniacal gas, 324
- Ammoniacal salts, 654
- Ammoniaco-magnesian phosphate, 1206
- Ammonium, 326, 694
  - ferrocyanide of, 731
  - sulpho-cyanide of, 746
  - oxide of, 326
- Ammoniuret of copper, 608
- Amygdaline, 802
- Analysis qualitative, 1227
  - quantitative, 1232
- Analytical chemistry, 1223
  - division of the subject, 1223
- Anemonine, 1102
- Anhydrite, 604
- Aniline, 1145, 1153, 1154
- Animal chemistry, 1207, 1222
  - oils and fats, 1063
  - jelly, 1193
  - heat, 1212
  - life distinguished from vegetable, 1212
- Animals, changes which occur during the life, growth, and nutrition of, 1207, 1212
- Anthracene, 1182
- Anthracite, 1176
- Antiarine, 1121
- Antimonialis, pulvis, 497

- Antimoniates, 497
- Antimonio-sulphurets, 666
- Antimonites, 497
- Antimony and its compounds, 493
  - butter of, 497
  - regulus of, 493
  - argentine flowers of, 493
  - glass, crocus, and liver of, 499
  - alloys of, *vide* Alloys
  - golden sulphuret of, 499
  - oxychloride of, 494
  - tartrate of, and potash, 1015
- Apatite, 632
- Apparatus, Nooth's, 237
- Appetite affected by external temperature, 1213
  - diminished by warm clothing, 1213
- Aqua fortis, 227
  - regia, 280
- Aqueous vapour, elastic force of at different temperatures, table of, 1248
- Arbor Dianæ, 536
  - Saturni, 522
- Archil, 1131
- Aricine, 1159
- Arrangement of the work, 6
- Arrow-root, 1170
- Arseniates, 635
- Arsenites, 638
- Arsenic and its compounds, 455
  - white oxide of, 455
  - tests of, 458
  - alloys of, *vide* Alloys
  - fuming liquor of, 464
- Arsenio-sulphurets, 661
- Arseniuretted hydrogen, 465
- Arterial membrane, 1194
- Asarine, 1102
- Asparagine, 1150
- Atmospheric air, 205
  - effects of organic life on, 1208
  - chemical properties of, 210
  - physical properties of, 205
  - analysis of, 208
  - weight of, 205
- Atom, definition of, 168
- Atomic theory, Dalton's view of, 167
- Atomic weights, 169
- Atropine, 1165
- Attraction, chemical, *vide* Affinity, 139
  - cohesive, 3
  - terrestrial, or gravity, 3
  - electric, 75
- Aurates, 540
- Auro-chlorides, 668
- Azobenzide, 795
- Azobenzoide, 801
- Azobenzule, 797
- Azoerythrine, 1133
- Azolitmine, 1133
- Azote, 203
- Azotized substances common to the vegetable and animal world, 1183

B.

- Baldwin's phosphorus, 71
- Balsam of Peru, 823
  - oil of, 823
  - of Tolu, 824
- Balsams, 1105
- Barilla, 647
- Barley, malting, 943
- Barium and its compounds, 388
  - sulphur salts of, 568, 657
  - haloid salts of, 667
  - hydrate of, 389
  - ferrocyanide of, 734
- Baryta or barytes, 388
  - tests of, 389
- Baryta, alloxanate of, 765
  - thionurate of, 770
  - hyposulphobenzoate of, 791
  - hyposulphobenzidate of, 794
  - sulphate of, 604
  - nitrate of, 618
  - nitrite of, 621
  - chlorate of, 622
  - arseniate of, 637
  - carbonate of, 649
  - metaphosphate of, 635
- Baryto-calcite, 652
- Bases, a table of those for the discovery of which directions are given in section on chemical analysis, 1227
  - tests used for the discovery of, and the modes of applying them, 1228.
- Bavarian beer, 875
- Bell-metal, 563, *vide* Alloys
- Benzamide, 787
- Benzhydramide, 797
- Benzilates, 801
- Benzile, 800
  - hydrocyanate of, 800
- Benzimide, 798
  - hydrocyanate of, 799
- Benzoates, 782
- Benzoic ether, 857
- Benzoinamide, 799
- Benzoine, 798
  - hydrocyanate of, 799
- Benzole, 793
  - chloride of, 795
- Benzone, 796
- Benzule, 779
  - constitution of the compounds of, 807
  - hyduret of, 785
  - formation of, from bitter almonds, 804
  - chloride of, 785
  - bromide of, 786
  - iodide of, 786
  - sulphuret of, 786
  - cyanide of, 787
  - benzoate of hyduret of, 789
  - table of compounds of, 780
  - appendix of, 803
- Berberine, 1169
- Berlin or Prussian blue, 740
- Beta orceine, 1133
- Bibromisatine, 1139
- Bromisatine, 1139
- Bile and biliary calculi, 1200, 1202
  - true functions of, 1213
  - formation of, 1214
- Bismuth or wismuth and its compounds, 504
  - magistery of, 505
  - butter of, 506
  - alloys of, *vide* Alloys
- Bitter principle, 1118, 1122
  - almonds, oil of, 779
- Bitumen, 1182
- Black dyes, 999
- Black flux, 1011
- Black lead, 435
- Black oxide of iron, 429, 430
  - copper, 516
- Bleaching, 275
- Bleaching powder, 275
- Blende, 437
- Block tin, 442

- Blood, 1191
  - analysis of, 1192
  - cruor or crassamentum of, 1191
  - coagulation of, 1191
  - serum of, 1192
  - serosity, 1192
  - fibrin of, 1188
- Blowpipe, with oxygen and hydrogen, 195
- Blue, Prussian or Berlin, 740
- Blue, Saxon, 1146
- Blue dyes, 1117
- Blue vitriol, 608
- Boa constrictor, urine of, 759
- Bodies, isomorphous, 591
  - isomeric, 183
  - plesiomorphous, 595
- Boiling point of liquids, 46
- Bone earth, 631, 1206
- Bones, 1197
- Borates, 642
- Borax, 262, 642
- Boro-fluorides, 678
- Boron and its acid, 261
  - terchloride of, 293
- Brain, analysis of, 1195
- Bran, valuable as a manure, 112
- Brass, 653
  - brazing, 653
- Breziline, 1116
- Bromal, 894
- Bromates, 627
- Brombenzoates, 793
- Bromides,
  - double, 677
  - of cyanogen, 744
- Bromine, 308
  - its compounds, 311
  - chloride of, 314
  - its attraction for metals, 360
- Brucine, 1167
- Brunswick green, 673
- Bryonine, 1121
- Butter, 1024
  - of antimony, 497
  - of zinc, 439

C.

- Cadmium and its compounds, 440
- Caffeine, 1169
- Calamine, 437
- Calcination, 356
- Calcium and its compounds, 394
  - sulphur salts of, 658
- Calcium, haloid salts of, 394
- Calculi, urinary, 1203
  - biliary, 1200, 1202
- Calculus, mulberry, 1205, 1206
  - bone earth, 1206
  - ammoniaco-magnesian, fusible, 1206
  - cystic oxide, 779
  - xanthic, 778
- Calomel, 528
- Caloric, *vide* Heat
- Calorimeter of Lavoisier and Laplace, 35
- Calx, 356
- Camera obscura, 63
- Camphone, 1030
- Camphor, 1029
  - oil of, 1029
  - artificial, 1029
- Camphorates, 1027
- Cannel coal, *vide* Coal
- Cantharadine, 1103
- Canton's phosphorus, 71
- Caoutchouc, 1103
  - volatile liquid of, 1104
- Capnomor, 1179
- Caramel, 930
- Carbon, 231
  - chlorides of, 288, 289, 290
  - its compounds with oxygen, 235
    - with hydrogen, 328
    - with nitrogen, 344
    - with sulphur, 347
- Carbo-sulphurets, 660
- Carbonates, general properties of, 643
  - double, 625
- Carbonic oxide, 239, 697
  - ether, 851
- Carbovinate of potash, 850
- Carburetted hydrogen, 329
- Carmine, 1147
  - blue, 1136
- Carnivora, food of, 1213
  - digestion of, 1217
- Cartilage, 1194
- Caseine, 1189
  - identical with legumine, 1189
  - occurs in many vegetables, 1190
- Cassius, purple of, 542
- Castor oil, 1063
- Castorine, 1084
- Catechine, 1001
- Catechu, 1000
- Cathartine, 1121
- Cedriret, 1179
- Celestine, 604
- Cetrarine, 1120
- Cerine, 1084
- Cerium, and its compounds, 503
- Cerosine, 1085
- Ceruse, 651
- Cetene, 982
- Cetine, 1082
- Cetule, 980
  - combinations of, 981
- Chalk, 649
  - stones, 759
- Chalybeate waters, 1239
- Charcoal, 232
  - animal, or ivory black, 232
  - property of absorbing gases, 233
  - antiseptic property of, 234
  - destroys colours in fluids, 234
- Chelidonine, 1163
- Chemical analysis, the different objects proposed in, 1223
  - exemplification of, 1223
  - quantitative and qualitative, 1223
  - directions for conducting, 1225
- Chemical decomposition, theory of, 130
  - action, changes that accompany it, of density, temperature, form and colour, 143
  - affinity or attraction, 139
  - symbols, 178
  - equivalents, 158
    - mode of ascertaining, 166
    - scale of, 166
  - formulæ, 178
  - symbols, table of, 179
- Chemical equivalents of elementary substances, table of, 1247
- Chemistry of agriculture, 1211
  - organic, 682
  - inorganic, 133
  - animal, 1207, 1222
- Cheese, *vide* Caseine
- Chinoidine, 1159

- Chinoiline, 1158
- Chlorates, 286, 621
- Chloral, 889
- Chloranilam, 1140
- Chloranilammon, 1140
- Chloranile, 1140
- Chlorides or chlorurets, 275
  - metallic, 358
- Chlorides with ammonia, 674
  - with phosphuretted hydrogen, 675
- Chlorides of carbon, 288
  - oxy-, 672
  - with double iodides, 676
- Chloride of sulphur, 290
  - phosphorus, 291
  - boron, 293
  - iodine, 306
  - bromine, 314
  - cyanogen, 743
  - nitrogen, 287
  - lime, 396
  - soda, 383
- Chlorine, 271
- Chlorine, its affinity for metals, 358
  - its compounds, 274, 275, 276
  - nature of, 273, 295
  - bleaching powers of, 275
  - disinfecting powers of, 275
  - theories of constitution of, 272
- Chlorine, and oil of cinnamon, 822
- Chlorindamit, 1141
- Chlorindine, 1140
  - bichlorisatyde, 1140
- Chlorindoptene, 1142
- Chlorisatine, 1137, 1138
  - bichlorisatine, 1137, 1139
- Chlorisatyde, 1139
- Chlorites, 623
- Chloroacetates, 892
- Chlorobenzide, 796
- Chlorocarbonic ether, 858
- Chlorocyan-aldehyde, 894
- Chloronaphthalase, 1181
- Chloronaphthalese, 1181
- Chloronaphthalise, 1181
- Chloronitrous gas, 294
- Chlorophane, 72
- Chlorophyll, 1117
- Chloropyromucic ether, 941
- Chlorosalicine, 817
- Chlorosaliculimide, 814
- Chlorurets, 275
- Cholesterine, 1083, 1196
- Chondrine, 1194
- Chromates, 639
  - of chlorides, 641
- Chromate of iron, 467
- Chromium and its compounds, 467
  - sulphate of, 608
- Chrome alum, 611
- Chrome yellow, 640
- Chrysammate of potash, 1149
- Chrysolepate of potash, 1149
  - of silver, 1149
- Chyle, 1199
- Chyme, 1199
- Cinchona bark, 1000
  - bases of, 1157
- Cinchonine, 1158
- Cinnabar, 533
- Cinnabar, factitious, 533
- Cinnamon, oil of, 820
- Cinnamule, 819
  - hydurets of, 822
- Cinnamates, 822
- Cinnameine, 823
- Citraconotates, 1008
- Citrates, 1003
- Citric acid, 1002
- Classification of chemical substances, 6
- Cleavage, 589
- Cloves, oil of, 1095
- Coal, 1176
  - gas, 1177
  - mines, fire-damp of, 331, 1176
  - wood or brown, 1175
  - mineral, 1176
  - caking, 1176
  - cannel, 1176
  - production of, 1176
  - gases, 1176
  - changes of, 1176
  - nitrogen contained in, 1176
  - action of heat on, 1177
  - splint, 1176
- Coagulation of the blood, *vide* Blood
- Cobalt and its compounds, 448
- Cyanides, 727
- Cobalto-cyanide of potassium, 740
- Cobalto-cyanides, 740
- Codeine, 1161
- Cocculus Indicus, principle of, 1168
- Cochineal, 1147
- Cohesive attraction, 3, 147
  - influence of, over chemical action, 146
- Cold, artificial methods of producing, 42, 51
- Colocynthine, 1120
- Colouring matter,
  - non-azotized vegetable, 1111
  - *vide* Blood
  - destroyed by chlorine and sulphuric acid, 1111
  - tendency to combine with alumina, with oxides of tin and other oxides, 1112
  - yellow, 1112
  - red, 1113
  - green, 1117
- Colours primitive, 67
- Coke, 232, 1177
- Columbin, 1121
- Columbium and its compounds, 490
- Combination defined, 155
  - utility of laws of, 162
  - laws of, 155, 156
- Combining proportions explained, 158
  - table of, 166
  - exemplifications of, 164
- Combustion, 186
  - theories of, 187, 188
  - spontaneous, *vide* Phosphuretted hydrogen and Pyrophorus
- Compound radical, 682
- Composition of bodies, 163
  - how determined, 166
- Conicine, 1155
- Conductor, prime, 83
- Conductors of heat, 12
- Conduction of heat, 11
- Cooling of bodies, 22
- Copal, 1109
- Copper-nickel, 452
- Copper and its compounds, 513
  - test of, 516
  - alloys of, *vide* Alloys
  - pyrites, 518
  - glance, 518
  - sulphates of, 608
  - nitrate of, 619

Copper, arsenite of, 639
  carbonate of, 651
  tinning of, 562
  copper-nickel, 452
  acetates of, 885
  black oxide of, 516
  white muriate of, 517
  sheathing, preservation of, 96
  fulminate of, 716
  ferrocyanide, 734
  sulphocyanide, 748
  hypo-sulphobenzidate, 795
  white, of the Chinese, 563
  ore, blue, 651
Cork, *vide* Suberic acid
Corydaline, 1169
Corrosive sublimate, 529
  tests of, 530
Count Rumford's mode of ascertaining conducting power of articles of clothing, 12
Cream of lime, *vide* Milk of lime, 395
  of tartar, 1010
Creosote, 879, 1178
Croconates of potassa, 707
Crocus of antimony, 499
Cryophorus, 51
Crystalline, 1146, 1154
Crystallization, 580
  systems of, 580, 584
  water of, 576
Crystallography, 580
  octohedral system of, 584
  square prismatic system of, 586
  right prismatic system, 587
  oblique, doubly oblique, and rhombohedral systems, 588
Crystals, simple form of, 581
  compound form of, 581
  angles, planes and edges of, in, 581
  structure of, 589
  cleavage of, 589
Cubebine, 1125
Cudbear, 1131
Curd, 1189
Cyamelide, 719
Cyanates, 710
Cyanic ether, 857
Cyanides, 724
  double, of metals, 729
Cyanogen, 344, 709
  compounds of, 709
  chlorides of, 743
  iodide of, 745
  bromide of, 744
  bisulphuret of, 745
  sulphuret of, 745
Cyanogen and its compounds, products of decomposition of, 749
  and carbonic oxide, hypothetical compounds of, 758
  and water, 749
  and ammonia, 749
  and hydrosulphuric acid, 757
Cyanurates, 718
Cyanurets, metallic, (or Cyanides,) 724
  double, 729
Cyanuret, red, of potassium and iron, 732
Cyclamine, 1123
Cystic oxide, calculus, 779, 1209

D.

Dammar, 1109
Daguerréotype, 69
Daturine, 1164
Dead Sea, analysis of its water, 1242
Decay of wood, 1175
  prevented by antiseptics, 1175
Decomposition, simple, 140
  double, 142
Decrepitation, 579
Definite proportions, doctrine of, *vide* Equivalents
Deflagration, 615
Deliquescence, 575
Delphine, 1167
Density, 52
Dephlogisticated air, *vide* Oxygen
  marine acid, *vide* Chlorine
Derbyshire spar, 519
Detonating powders, 714
Dew, formation of, 21
Dew-point, 55
Dextrine, 921, 1172
Diamond, 231
  probable origin of, 1175
Diastase, 943, 1172
Differential thermometer, 29
Digestion, the process of, explained, 1217
  respective action in, of gastric juice, hydrochloric acid, and oxygen, 1218
Dioxides, 164
Disinfecting liquor, 275
Distilled waters, 1088
Distillation by descent, 437
Drying oils, 1064
Dutch gold, 563
Dyes, 1111

E.

Earths, pure, 369
  metallic bases of, 104
  siliceous, 264
  alkaline, 369
  aluminous, 403
Earthy sulphates, mode of analysing, 1234
Earthy minerals, analysis of, containing silica, iron, alumina, manganese, lime and magnesia, 1237
Ebullition, 46
Efflorescence, 576
  influence of, over affinity, 149
Eggs, 1186
Elaidates, 1058
Elaldehyde, 871
Elastic gum, 1103
Elasticity, its effects on chemical affinity, 149
  of vapours, 53
Elaterine, 1120
Electric attraction, 75
  repulsion, 75
  excitement, causes of, 80
  intensity, 88
  currents, 113
Electrics, positive, 130
  negative, 130
Electrical battery, 84
  accumulation, laws of, 89
  machine, 80
  unit jar, 88
Electricity, 75
  elementary facts of, 75
  conductor and non-conductors of, 76
  vitreous or positive, 77
  resinous or negative, 77

- Electricity, theories of, 79
  - induction of, 83
  - of atmospheric, 82
  - identical with lightning, 93
  - historical notice relating to, 92
  - velocity of, 92
  - light of, 92
  - condenser of, 84
- Electro-chemical decomposition, theory of, 117
  - theory, 123
- Electrodes, 118
- Electro-dynamics, 107
- Electro-magnetism, 111
- Electrometer, balance, 87
  - quadrant, 86
  - gold leaf, 85
  - torsion, 86
- Electrolyte, 119
- Electro-negative and positive elements, 127
- Electrophorus, 85
- Electroscopes and electrometers, 85
- Elements, 178, 179
- Elementary substances, chemical equivalents of, 158
- Emetic tartar, 1014
- Emetine, 1168
- Empyreal air, *vide* Oxygen
- Emulsion, 804
- Emulsine, 804, 1130
- Enamel of teeth, 1197
- Epidermis, 1195
- Epithelium, 1195
- Epsom salts, 605
- Equivalent, chemical, 158
  - scale of, 159
- Eremacausis, 617, 1175
- Ergotine, 1122
- Erythrine, 1130
- Erythroprotide, 1185
- Erythroleine, 1133
- Erythrolitmine, 1133
- Erythronium, 475
- Essential oils, 1086
  - salt of lemons, 702
  - non-oxygenated, 1089
  - oxygenated, 1093
  - containing sulphur, 1099
- Ethal, 980
- Ether, 825
  - theory of the formation of, 825
  - constitution of, and its compounds, 911
- Ether, acetic, 879
  - oxalic, 852
  - chloric, 831
  - hydriodic, 832
  - hydrochloric, 831
  - oxidized, 828
  - hydrobromic, 832
  - sulphuric, 825
  - methylic, 953
  - muriatic, 831
  - heavy muriatic, 893
  - carbonic, 851
  - cyanic, 857
  - benzoic, 857
  - chlorocarbonic, 858
- Etherine, sulphate of, 862
- Etherole, 862
  - sulphovinate of, 861
  - sulphate of, 863
- Ethionate of baryta, 864
- Ethiop's mineral, 533
  - per se, 526
- Ethule or Ethyle, 825
  - with oxygen, 825
  - with water, 828
  - and chlorine, 831
  - bromide of, 832
  - iodide of, 832
  - sulphuret of, 833
  - compounds of, sulphuret of, 835
  - bisulphuret of, 835
  - seleniuret of, 836
  - cyanide of, 836
  - sulphocyanide of, 836
  - oxide of, and oxalic acid, 852
  - double salts of oxalic acid, with oxide of, 853
  - oxalate of, with ammonia, 854
  - bicarbosulphate of oxide of, 855
  - oxide of, and hydrated cyanic acid, 857
  - oxide of, and benzoic acid, 857
  - compounds of, of uncertain constitution, 885
  - salts of, 837
  - oxide of, and sulphuric acid, 838
  - double salts of the sulphate of oxide of, 484
  - oxide of, and phosphoric acid, 846
  - phosphate of oxide of ethule with metallic oxides, 847
- Ethule, oxide of, and arsenic acid, 848
  - oxide of, with nitric acid, 848
  - oxide of, with hyponitrous acid, 848
  - oxide of, with carbonic acid, 850
  - carbonate of oxide of, 851
  - sulphate of oxide of, 861
- Eupione, 1177
- Evaporation, 49
  - circumstances influencing, 49
  - cause of, 54
  - limit to, 50
  - Leslie's method of freezing by, 50
- Excrements, solid, 1203
  - ashes of, 1203
- Expansion of solids, 26
  - force of, in solids irresistible, 24
  - of liquids, 25
  - of gases, 28
  - table of the expansion of different bodies, 25
  - increasing ratio of, in fluids, 26
  - of some fluids by cold, 26
  - of some solids, 27
- Extractive matter, 1118
- Extractum saturni, 885
- Eye, action of, on light, 63

F.

- Factitious cinnabar, 533
- Farina, 1170
- Fat animal, how produced, 1220
- Fat of animals, 1081
- Feathers, 1195
- Fecula, 1170
- Ferment, 946
- Fermentation, 945
  - viscous, 947
  - acetous, 874
  - panary, *vide* vinous
  - putrefactive, 946
  - vinous, 944
  - saccharine, 943
- Ferrid-cyanogen, 738
- Ferro-cyanurets, 731
- Ferro-cyanides, 731
  - with basic metals, 737
  - constitution of, 742

Ferro-cyanide of potassium and iron, &c. 737
Ferro-sesquicyanurets, 735
Fibre, woody, 943
Fibrine, 1187
  of the blood, 1188
  identity of vegetable and animal, 1188
Filter, 1225
Filtration, 1225
Fire-damp of coal mines, 331, 1176
Fixed bodies, 44
Fixed air, 235
Fixed oils, 1063
Flame, *vide* Combustion and Carburetted hydrogen
Flesh, 1193
Flint, 265
Flowers of sulphur, 242
  argentine of antimony, 493
Fluoborates, 321
Fluidity caused by heat, 39
  heat of, 39
Fluosilicates, 324, *vide* Salts
Fluorides, metallic, 318
Fluorides, double, 677
  oxy-, 681
Fluorine, 316
  its attraction for metals, 360
  theories relating to, 319
Fluor spar, 319
Flux, white and black, 1011
Fly powder, 456
Food of plants, 1208
Formiates, 669
Formobenzoates, 789
Formomethylal, 965
Formule, 954
  compounds of, 972
Fraxinine, 1124
Freezing mixtures, 42
  tables of, 42
Freezing in vacuo, Leslie's method of, 50
Friction, heat produced by, 58
  electricity excited by, 75
Frigorific mixtures with snow, table of, 42
Fruits, ripening of, 944
Fulminates, 714
  of copper and zinc, 716
Fulminating gold, 541
  mercury, 715
Fulminating platinum, 548
  silver, 716
Fumaramide, 1022
Fuming liquor of Libavius, 446
  of Boyle, 656
  of arsenic, 464
Fusible metal, 354
Fusion,
  watery, 576
  point of, 354

G.

Galena, 519
Gallates, 996
Gall-nuts, 999
Galvanic battery, 100, 101
Galvanism, 93
  how developed, 93
  effects of, 104
  chemical agency of, 116
  electrical agency of, 105, 118
  connection of, with magnetism, 113
  theories of its production, 123
  magnetic effects of, 106
  chemical theory of, 124
Galvanometer, 94, 108
Gases, 44
  constitution of, with respect to heat, 56
  pressure required to liquefy, 57
  table of refractive indices of, 62
  table of, exhibiting their distinctive properties, 1231
  become incandescent when strongly heated, 70
  mode of finding the specific gravity of, 134
  condensation of, 57
  law of expansion of, 28
  diffusion of, 213
  formula for correcting the effects of heat on, 28
  their bulk influenced by moisture, and the formula for correcting its effects, 53, 54
Gases, qualitative analysis of, 1231
  absorption of, by charcoal, 233
  mode of drying, 56
Gastric juice, 1199
  the action of, in digestion, 1218
Gelatine, 1193
  how produced, 1219
  sugar, 1193
Gelatinous tissue, 1193
Gentianine, 1119
Germination, 1119, 1207
Gibbsite, 405
Glance silver, 537
  copper, 518
Glass, various kinds of, 266
  of antimony, 499
  of borax, 643
Glauberite, 609
Glauber salts, 603
Glaucopicrine, 1164
Globuline, 1191
Glucina, 407
  test of, 409
Glucinium and its oxide, 407
Glue, 1193
Gluten, 1188
Glycerine, 986
Glycerule, 986
  salts of, 988
Glycicoll, 1193
Gold and its compounds, 538
  fulminating compound of, 540
  ethereal solution of, 542
  alloys of, 565
  haloid salts of, 668
Golden sulphuret of antimony, 499
Gong, Chinese, 653
Goulard's extract, 759, 885
Gouty concretions, 759
Grain tin, 442
Graphite, 435
Gravel, urinary, 759
Gravitation, 2
Gravity, effect of, on chemical action, 153
  modes of determining, 133
Green, Scheele's, 459, 639
  mineral, 651
  Brunswick, 673
Green vitriol, 606

Growth of plants, 1207
Guaiacine, 1123
Guano, 759, 1211
Gum, 1174
  elastic, 1103
  tragacanth, 1174
Gypsum, 604

H.

Haarkies, 454
Hæmatite, brown and red, 424
Hæmatosine, 1191
Hæmatoxylin, 1164
Hair, 1195
Haloid salts, 569, 667
Harmaline, 1168
Hartshorn, spirit of, 324
Heat, 9
  animal, how produced, 1212
  definition of, 9
  nature of, 9
  communication of, by contact, 10
  conduction of, 11
  conductors of, table of, 12
  of fluidity, 40
  slow conductors of, 12
  conveyed by liquids, 12
  effect of upon liquids, 13
  effect of upon gases, 13
  radiation of, 14
  what surfaces best suited for radiation of, 15
  radiation of, affected by colours, 15
  absorption of, affected by colours, 17
  has different degrees of refrangibility, 19
  polarization and double refraction of, 20
  essential to vital action, 22
  influence of upon vegetation, 22
  dimensions and forms of bodies influenced by, 23
  effect of, on chemical action, 23
  quantity of, transmitted by different bodies, 18
  relation of, to light, 74
Heat emitted during combustion, 191
  latent, 35, 40
  free, 35
  luminous, 70
  non-luminous, 17
  effects of, 22
  expansion by, 24
  expansion of solids, 24
  expansion of liquids, 25
  expansion of gases, 28
  exception to the law of expansion by, 27
  how conducted by liquids and gases, 13
  specific, 34, 36, 37
  specific, table of, 38
  laws of distribution by radiation, 14
  capacities of bodies for, 34
  sensible and insensible, 35
  sources of, 58
  radiated, 14
  reflection of, 15
  absorption of, 16
  transmission of, 17
  theory of, by Prevost and Pictet, 20
  application of Prevost's theory to the formation of dew, by Dr. Wells, 21
Heavy spar, 604
Helenine, 1101
Herbivora, food of, 1213
Hippurates, 790
Hogslard, 1082
Homberg's pyrophorus, 610
Horn, 1195
  silver, 537
  quicksilver, 528
  lead, 524
Horny matter, membraneous and compact, 1195
Humus, 915, 1175, 1210
  true effect of, in the nourishment of plants, 1209, 1210
Hydracids, 682, 688
Hydramide, 693
Hydrargo-chlorides, 667
Hydrarsine, 910
Hydrate of an acid explained, 690
Hydrates, nature of, 199
Hydriodates, 301
Hydro, how employed, 199
Hydrobenzamide, 796
Hydrocarburet, 329
Hydrochlorates, 653
Hydrocobalto-cyanates, 741
Hydrocyanates, 724
Hydroferrid-cyanates, 739
Hydrogen, 192
  preparation of, 192
  properties of, 193, 200
  compounds of, with sulphur, 333
  compounds of, with phosphorus, 339
  oxidation of, 193, 194
  peroxide of, 200
  arseniuretted, 465
  carburetted, 328
  and carbon, compounds of, 328
  and carbon, new compounds of, 329
  and nitrogen, 324
  and potassium, 379, 695
  seleniuretted, 338
  sulphuretted, 333
  persulphuret of, 336
  with metals, 368
  phosphuretted, 340
  perphosphuretted, 340
  salts of, 657
  aurochloride of, 668
  phosphuretted, chlorides with, 765
  platino-biniodide of, 677
Hydrogurets, or hydurets, of metals, 368
Hydrosalts, 653
Hydrosulphurets, 658
Hyduret of benzule, 785
Hyduret of cinnamule, 822
Hyduret of spirole, 808
Hygrometers, 54
Hyoscyamine, 1164
Hyponitrite of oxide of ethule, 848
Hyposulphobenzoates, 791
Hyperoxymuriates, 286

I.

Ice, *vide* Water
Imperatorine, 1123
Imponderables, 9
  influence of, over chemical action, 154
Incandescence, 70

Indigo, 1133
  white, 1134
  blue and white, composition of, 1134
  action of sulphuric acid on, 1135
  products of oxidation of, 1137
  products of the action of alkalies on, 1144
  commercial, 1145
  gluten of, 1145
  brown and red, 1145
  red deoxidized, 1146
  soluble, 1146
Induction, electric, 83
  magneto-electric, 113
Inflammable air of marshes, 329
Ink, marking, 620
  sympathetic, 450
Insolubility, influence of, on affinity, 147
Insulators, electrical, 76
Inulin, 1173
Iodates, 625
Iodides, or iodurets, 299
Iodides, metallic, 359
  of hydrocarbon,
  double, 676
  oxy-, 677
  of cyanogen, 745
Iodine, 297
  test for, 300
  compounds of, 300
  oxide of, 303
  chlorides of, 306
  and alcohol, 894
  bromide of, 315
  attraction of, for metals, 359
Ipecacuanha, 1168
Iridio-chlorides, 671
Iridium and its compounds, 553, 557.
Iron and its compounds, 424
  ores of, 424
  cast, 426, 436
  rusting of, 427
  pyrites, 434
  malleable, 426
  black oxide of, 427
  red oxide of, 427
  cyanide of, 726
  ferrocyanide of, 734
  ferrid-cyanide of, 740
  benzoate of, 784
  pyrites, magnetic, 435
  sulphates of, 606
  alum, 611
  meteoric, components of, 424, 452
Iron, chromate of, 467
  carbonate of, 650
  ferrosesquicyanuret of, 734
  alloys of steel, 564
Iron and manganese, analytical mode of separating, 1235
Isatine, 1137
Isatyde, 1138
Isethionates, 865
Isinglass, 1193
Isomeric bodies, 183
Isomorphism, 591
Ismorphous substances, table of, 593
Ivory black, 232, 1197

J.

Jelly, animal, 1193
Jervine, 1166

K.

Kalium and Kali, 373
Kakodule, 907
  compounds of, 907
Kelp, 647
Kermes mineral, 499
Kidneys, office of, 1219
Kermes, 1147
Kinates, 1023
King's yellow, 466
Kino, 1000
Kinoyle, 1024
Komenates, 992
Kupfernickel, 452

L.

Labarraque's soda liquid, 275
Lac, 1109
Lactates, 951
Lactine, 935
Lactucine, 1122
Lakes, 1112
Lamp, safety, 331
Lantanium, 503
Lapis causticus, 374
  infernalis, 620
  lazuli, 385
Lard, *vide* Fats
Latent heat, 35, 40
Laurel-water, 804
Laws of combination, 155, 156
Laws of combination in multiple proportions, 158
  volumes, 171
  of the distribution of radiant heat, 14
Lead and its compounds, 519
  white, 522, 662
  horn, 524
  ceruse of, 522, 662
  nitrate of, 619
  nitrite of, 621
  phosphate of, 633
  arseniate of, 638
  carbonate of, 652
  oxychloride of, 673
  oxy-iodides of, 677
  oxyfluoride of, 681
  acetate of, 884
  mellitate of, 709
  cyanate of, 713
  ferrocyanide of, 734
  cobaltocyanide of, 741
  sulphocyanide of, 748
  thionurate of, 770
  tests of, in wine, 522
  benzoate of, 784
  hyposulphobenzoate of, 792
  malate of, 1020
  alloys of, 562
Leather, 1193
Lecanorine, 1127
Legumine, 1189
Lemons, acid of, 702
  essential salt of, 702
Lenses, achromatic, 66
  of the eye, 64
Lepidolite, 386
Leucine, 1185
Leyden jar, 83
Libavius, fuming liquor of, 446
Ligaments, 1194
Light, theories of, 58
  diffusion of, 59
  ordinary ray of, 65
  extraordinary ray of, 65
  reflection of, 60
  refraction of, 61
  refraction, double, of, 64
  polarized, 65
  decomposition of, 65
  calorific rays of, 67
  prismatic colours of, 66
  chemical rays of, 69
  magnetizing rays of, 70
  terrestrial, 70
  sources of, 70
  law of its distribution, 59
  velocity of, 60

- Light, laws of reflection of, 60
  - laws of refraction of, 62
  - table of refractive indices, 62
  - dispersion of the rays of, 66
  - calorific, rays of, 67
  - colorific rays of, 66
  - illuminating power of different rays of, 67
  - relation of, to heat, 74
  - coloured, emitted by different substances, 71
- Lightning, 93
- Lignine, 1174
- Lignone, 980
- Lime, or quicklime, 394
  - thionurate of, 770
  - benzoate of, 783
  - fluate of, 319
  - water, milk of, and hydrate of, 395
  - slaked, 395
  - chloride of, 396
  - sulphate of, 604
  - sulphite of, 614
  - nitrate of, 618
  - phosphates of, 631
  - arseniate of, 638
  - carbonate of, 649
  - carbonates, double, of, 652
  - oxalate of, 703
  - acetate of, 882
  - -stone, 649
- Lime and magnesia, analytic mode of separating, 1233
- Liquids become incandescent at high temperatures, 70
- Liquefaction, 39
  - attended by disappearance of heat, 39
- Liquids, expansion of, by heat, 25
  - conducting power of, 12
- Liquor silicum, 266
- Liriodendrine, 1120
- Litharge, 521
- Lithates, *vide* Urates,
- Lithia, or, Lithion, 386
  - sulphate of, 603
  - tests of, 386
- Lithium and its compounds, 386
  - hydrosulphuret of, 659
- Lithium,
  - carbosulphuret of, 661
  - arseniosulphuret of, 664
  - molybdosulphuret of, 665
  - hydrargo-chlorides of, 667
- Litmus, 1131
- Liver, office of the, 1219
- Liver of antimony, 499
  - of sulphur, 362
- Luna cornea, 537
- Lunar caustic, 536
- Lupuline, 1122
- Lymph, 1203

M.

- Madder, purple, red, orange, &c., 1162
- Madder lake, 1116
- Magnesia, 399
  - tests of, 400
  - sulphate of, 605
  - nitrate of, 618
  - phosphates of, 632
  - carbonate of, 649
  - oxalate of, 704
- Magnesian limestone, 652
  - mode of analysing, 1233
- Magnesite, 649
- Magnesium, 399
  - and its compounds, 399
  - hydrosulphuret of, 658
  - arseniosulphuret of, 660
  - haloid salts of, 667
- Magnet, horseshoe, 110
- Magnetic iron pyrites, 435
- Magnetism, electro-, 107
- Magneto-electric induction, 110
- Malachite, 651
- Malates, 1019
- Manures, explanation of their nature and their operation, 1210
- Manganese and its compounds, 414
  - sulphate of, 606
  - haloid salts of, 668
  - alum, 612
- Manganesium, or Manganium, 414
- Manna and Mannite, 948
- Marble, 649
- Manipulations in analytical processes, 1224
- Marble or carbonate of lime, mode of analysing, 1232
- Margarates, 1039
- Margarine, 1064
- Margarone, 1041, 1047
- Massicot, 521
- Mastic, 1109
- Matter, chemical properties of, 4
  - influence of quantity of, over affinity, 151
- Meconates, 990
- Meconine, 1124
- Melam, 753
- Melamine, 754
  - and acids, 755
- Melampyrine, 1124
- Mellitates, 708
- Mellon, 750
- Mellon and potassa, 752
- Mellonide of potassium, 751
- Membranes, 1193
- Menispermine, 1168
- Mercury and its compounds, 525
  - amalgams of, 561
  - fulminating compound of, 715
  - sulphates of, 608
  - nitrates of, 619
  - carbonates of, 651
  - oxychloride of, 674
  - acetate of, 886
  - chloramide of, 696
  - cyanide of, 727
  - ferrocyanide of, 735
- Mercaptan, 683, 833
- Mercaptide of gold, 835
- Mesitylene, 902
  - action of chlorine on, 905
- Mesitule, 901
  - its compounds, 901, 903
- Metacetone, 931
- Metaldehyde, 872
- Metallic combinations, 558
  - bases of the alkaline earths, 388
  - bases of the alkalies, 371
- Metallic sulphocyanides, 747
- Metals, 351
  - general properties of, 351
  - alloys of, 355

Metals, oxidation of, 356, 357
  alkaline or alkaligenous, 369
  table of discovery of, 351
  table of specific gravity of, 352
  malleability of, 353
  ductility of, 353
  crystallization of, 354
  tenacity of, 353
  hardness of, 354
  structure of, 354
  native state of, 355
  volatility of, 355
  alloys of, 355
  affinity of, 355
  action of heat on, 354
  action of electricity on, 351
  fusibility of, table of, 354
  reduction of, 357
  compounds of, with
    chlorine, 358
    iodine, 359
Metals with bromine, 360
    fluorine, 360
    sulphur, 360
    selenium, 364
    cyanogen, 364
    phosphorus, 368
    carbon,
    hydrogen, 368
    nitrogen, 368
    classification of, 368
Metaphosphates, 635
Meteoric stones, 424
Methule, 952
  hydrate of oxide of, and other compounds of, 952, 955
  salts of, 957
  compounds of, of uncertain constitution, 963
  products of decomposition of, 964
  action of chlorine on compounds of, 976
Methylal, 966
Methylene, bihydrate of, 953
Milk, 1189
  sugar of, 1198
  cause of coagulation of, 1189
  analysis of, 1198
Minderreus, spirit of, 880
Mineral chameleon, 421
  green, 651
  yellow, 674
Mineral waters, analysis of, 1237
  denominations of, 1238
  tables of the composition of, 1244
Minerals, needful to plants, are also indispensable to animals, 1217
Minium, 522
Molasses, 927
Molecules, 170
Molybdates, 485
Molybdenum and its compounds, 483
Molybdo-sulphurets, 655
Mordant, 446
Morphia, or Morphine, 1159
  Pseudo-morphine, 1162
Mouldering, 1175
Mucates, 938
Mucus, 1203
Mudarine, 1121
Mulberry calculus, *vide* Calculus
Multiples, law of, 155, 160
Murexan, 778
Murexide, 775
Muriates, 654
Muriatic ether, heavy, 893
Muscular tissue or fibre, 1192
Muscular motion dependent upon transformation of the tissues, 1213
Mustard, oil of, 1099
Myroxiline, 824
Myricine, 1084
Myriospermine, 824

N.

Nails of animals, 1195
Naphtha from coal tar, 1182
Naphthalamide, 1182
Naphthalimide, 1182
Naphthaline, 1180
Naphthalose, hydrochlorate of, 1181
Narceine, 1162
Narcotine, 1163
Natrium, 383
Natron, 383
Nervous matter, 1195
  contains phosphorus, 1195
Nervous system how affected by vegetable alkalies, 1220
Neutral salts, characters of, 574
Neutralization, 144
Nickel and its compounds, 452
  sulphates of, 607
Nicotianine, 1102
Nicotine, 1154
Night-soil, neglect of, as manure, 1211
Nitrates, 614
  table of, 616
Nitrate of soda, as a manure, 1212
Nitre, 616
Nitric oxide gas, 218
Nitrites, 621
Nitrobenzide, 795
Nitrobenzule, 797
Nitrous ether, 848
Nitronaphthalase, 1181
Nitronaphthalese, 1181
Nitronaphthalise, 1181
Nitrogen, 203
  teriodide of, 307
  sulphuret of, 349
Nitrogen gas,
  properties of, 204
  oxides of, 205
  protoxide of, 215
  binoxide of, 218
  quadrochloride of, 287
  compounds of, with carbon, 344
Nomenclature, 135
Nut galls, 999
Nutrition of animals, 1212
  by what substances effected, 1213

O.

Oil of vitriol, 245
  of wine, 862, 1032
  gas, 1067
  of mustard, bases of, 1156
  of olefiant gas, 896
  animal, 1063
  fixed, 1063
Oils, drying, or siccative, 1079
  volatile, or essential, 1086

Oil, vegetable, 1063, 1079
Oil of turpentine, 1089
  of juniper, 1091
Oils and fats occurring in nature, 1079
  fish, 1079
  liquid fat, 1080
  solid fat, 1080
Oils, sweet, principle of, 986
  occurring in nature, 1079
Ointment, 1078
Olefiant gas, 895
Oleine, 1064
Olive oil, 1080
Olivile, 1125
Olivine, 1125
Omichmyle, oxide of, 1205
Opium, active principle of, 1159
Orceine, 1128
Orcine, 1128
Organic chemistry, 682
  substances, character of, 683
  bases, 1151
Organic acids, theory of, 686
  classification of, 691
Orpiment, 466
Osmio-chlorides, 671
Osmium and its compounds, 555
  test of, 556
Oxalates, 701
Oxalovinates, 853
Oxamethane, 854
Oxamethylane, 961
Oxamide, or Oxalamide, 705, 961
Oxichloride of acetule, 887
Oxichloronaphthalose, 1181
Oxidation, 186
Oxide of ammonium, 694
Oxide, carbonic, 235
Oxides, 136
  nomenclature of, 136
Oxidum manganoso-manganicum, 419
Oxidum ferroso-ferricum, 430
Oxygen, 184
  preparation of, 184
  properties of, 185
  necessary to respiration, 187
Oxyhydrogen blow-pipe, 195
Oxymuriate of potash, 622
Oxymuriate of lime, 396
Oxiodine, 304
Oxychlorides, 672
Oxyfluorides, 681

P.

Palladio-chlorides, 670
Palmitine, 1037
Palmine, 1073
Palladium and its compounds, 549
  cyanide of, 729
Panary fermentation, *vide* Vinous
Pancreatic juice, 1199
Papin's digester, 47
Paracyanogen, 345, 750
Paraffine, 1179
Paramenispermine, 1168
Paramorphine, 1162
Paranaphthaline, 1182
Parilline, 1122
Particles, integrant and component, 4
Patent yellow, 674
Pearlash, 645
Perchlorates, 622
Peruvine, 823
Petroleum, 1182
Peucedanine, 1123
Pewter, 562
Pharmacolite, 638
Phillyrine, 1124
Phloretine, 818
Phloridzeine, 819
Phloridzine, 818
Phlogiston, 192
Phosphates, 627
Phosphorescence, 70
Phosphoric ether, 846
Phosphorus, 252
  iodides of, 307
  bromides of, 315
  combinations of, with oxygen, 255
    with hydrogen, 340
  chlorides of, 291
  solar, 72
  sulphuret of, 348
  Baldwin's 71
  Canton's, 71
  Homberg's, 71
Phosphuret of nitrogen, 346
Phosphurets, metallic, 367
Phosphuretted hydrogen gas, 340
  salts of, 657
  chlorides with, 675
Photography, 69
Photometer, 73
Picamar, 1179
Picrolichenine, 1120
Picrotoxine, 1168
Pigmentum nigrum oculi, 1195
Pinchbeck, 563
Piperine, 1168
Pitchblende, 501
Pitch, mineral, 1108
Pit-coal, 1176
Pittacal, 1179
Plants, growth of, 1207
  derive ammonia and carbonic acid gas from the air, 1208
  digestion of, 1208
  food of, 1209
  respiration of, 1208
Plaster of Paris, 605
Plasters, 1078
Platino-chlorides, 669
Platinum and its compounds, 544
  a powerful oxydizing agent, 546
  spongy, 545, 547
  fulminating powder of, 548
  alloys of, 544
Plesiomorphism, 559
Plumbagin, 1123
Plumbago, 435
Polychrome, 1118
Populin, 1119
Porphyroxine, 1122
Potash, or pearlash, 645
Potash, or potassa, 373
  croconate of, 707
  cyanate of, 712
  cyanurate of, 719
  urate of, 761
  saliculite of, 811
  carbovinate of, 850
  hydrate of, 374
  solution of, 374
Potassa fusa, 374
  tests of, 376
  sulphates of, 602
  sulphite of, 614
  nitrate of, 616
  nitrite of, 620
  chlorate, oxymuriate, or hyperoxymuriate of, 622
  iodates of, 626
  phosphates of, 630
Potash, or potassa,
  arseniates of, 636
  arsenite of, 638
  chromates of, 639
  carbonates of, 644
  oxalates of, 702

- Potash, or potassa,
  - acetate of, 880
  - malate of, 1019
  - citrate of, 1004
  - tartrates of, 1010
  - tartrate of, and soda, 1013
  - triple prussiate of, 732
- Potassium and its compounds, 371
  - cyanide of, 725
  - ferro-cyanide of, 732
  - ferrid-cyanide of, 739
  - cobalto-cyanide of, 741
  - sulpho-cyanide of, 747
  - mellonide of, 751
  - sulphur-salts of, 658
  - haloid-salts of, 668
  - hydrosulphuret of, 658
  - sulphocyanuret of, 747
  - carbo-sulphuret of, 660
  - arsenio-sulphurets of, 663
  - molybdo-sulphuret of, 665
- Potato starch, 1170
  - oil of spirit of, 982
- Precipitate, red, 527
- Pressure, influence of, on the bulk of gases, 206
- Prism, 65
- Prismatic or solar spectrum, 66
- Proof-spirit, 830
- Proportions, definite, 155
  - combining, 156
- Proportions in which bodies unite, 153
- Proteine and its modifications, 1183, 1184
- Protide, 1185
- Prussian, or Berlin blue, 740
- Prussiates, *vide* Hydrocyanates
- Prussiate, triple, 730
  - of mercury, 735
- Pulvis antimonialis, 497
- Purple powder of Cassius, 542
- Pus, 1203
- Putrefaction, 946
- Putrefactive fermentation, 946
- Pyrites, iron, 434
  - copper, 518
- Pyrogallates, 998
- Pyrometer of Daniell, 32
  - Wedgewood, 32
- Pyrophorus of Homberg, 610
- Pyrophosphates, 633
- Pyroxylic spirit, 953

Q.

- Qualitative analysis, directions for performing, 1227
  - observations on, 1227
- Quantitative analysis, directions for performing, 1225
- Quantity, its influence on affinity, 151
- Quassiine, 1122
- Quicklime, 394
- Quicksilver, 525
  - horn, 528
- Quills, *vide* Feathers
- Quina, or Quinine, 1157

R.

- Radiation, *vide* Heat
- Radicals of organic acids, 693
- Radicals of organic bases, 693
- Rays of heat, angles of incidence and reflection of, 16
  - luminous, 18
- Realgar, 466
- Red lead, 522
  - antimony, 499
  - precipitate, 527
  - dyes, 1161
  - oxide of manganese, 416
  - oxide of copper, 515
- Reduction of metals, 357
- Rennet, 1189
- Resin of copper, 517
- Resineone, 1107
- Resinone, 1107
- Resin of aldehyde, 871
- Resins, 1105
- Respiration, 1212
  - of plants, 1208
- Rhodizonate of potassa, 706
- Rhodio-chlorides, 671
- Rhodium and its compounds, 551
- Rochelle salt, 1013
- Rouge, 1114
- Rutilene, 817

S.

- Sabadilline, 1166
- Saccharine fermentation, 920, 943
- Saccharum Saturni, 884
- Sacchulmine, 928
- Safety-lamp, Sir H. Davy's, 331
  - improvement of, by Messrs. Upton and Roberts, 333
- Sal-ammoniac, 654
- Salseparine, 1122
- Salicine, 816
- Salicule, 808
- Saliculimide, 811
- Saliculites, 811
- Salifiable base, 567
- Saliretine, 817
- Saliva, 1198
- Salivary matter, 1198, 1218
- Salt, common, 383
  - of Alembroth, 667
  - neutral, 144
  - of Seignette or Rochelles salt, 1013
  - of sorrel, 1010
  - Glauber's, 603
  - of lemons, 702
  - -petre, 616
  - spirits of, 276
- Salts, general remarks on, 566
  - nomenclature of, 136
  - classification of, 568, 574
  - affinity of, for water, 557
  - crystallization of, 581
  - double and triple, 596
  - deliquescent, 575
  - aqueous fusion of, 576
  - efflorescence of, 576
  - water of crystallization of, 576
  - decrepitation of, 579
  - plesiomorphism of, 559
  - isomorphous, 591
  - oxy-, 596
  - sulphates, 598
    - table of, 600
  - double, 609
    - table of, 600
  - sulphites, 614
  - nitrates, 614
    - table of, 616
  - cyanates, 710
  - nitrites, 621

Salts, chlorates, 621
  perchlorates, 622
  hypochlorites, 623
  iodates, 625
  bromates, 627
  chlorites, 623
  phosphates, 627
    table of, 628
  pyrophosphates, 633
  metaphosphates, 635
    table of, 635
  arseniates, 635
    table of, 637
  arsenites, 638
  chromates, 639
  chlorides, 276
  borates, 642
  carbonates, 643
    table of, 644
    double, 652
  hydro-salts, 653
  ammoniacal, 654
    table of, 654
  of phosphuretted hydrogen, 657
  sulphur-salts, 657
  hydro-sulphurets, 658
    table of, 658
  sulpho-cyanurets, 747
  carbo-sulphurets, 660
    table of, 660
  arsenio-sulphurets, 661
    table of, 661
  molybdo-sulphurets, 665
    table of, 665
  antimonio-sulphurets, 666
  tungsto-sulphurets, 666
  haloid-salts, 667
  hydrargo-chlorides, 667
    table of, 667
  auro-chlorides, 668
    table of, 668
  platino-chlorides, 669
    table of, 669
  palladio-chlorides, 670
  rhodio-chlorides, 671
  iridio-chlorides, 671
  osmio-chlorides, 671
  oxy-chlorides, 672
  chlorides with ammonia, 674
  chlorides with phosphuretted hydrogen, 675
  double iodides, 676
  oxy-iodides, 677
  double bromides, 677
Salts, double fluorides, 677
  boro-fluorides, 678
  silico-fluorides, 679
  titano-fluorides, 680
  oxy-fluorides, 681
  double cyanurets, 729
  ferro-cyanurets, 734
  ferro-sesquicyanurets, 737
  zinco-cyanurets, 738
  cobalto-cyanurets, 740
  oxalates, 701
  acetates, 879
  lactates, 950, 951
  of saccharic acid, 932
  mucates, 938
  pyromucates, 940
  methionates,
  formiates, 969
  meconates, 990
  komenates, 992
  pyrogallates, 998
  aconitates, 1007
  itaconates, 1007
  citraconates, 1008
  tartralates, 1016
  phocenates, 1026
  sabadillates, 1026
  cocoates, 1034
  sericates, 1035
  margarates, 1039
  stearates, 1041
  oleates, 1053
  sebates, 1056
  elaidates, 1057
  arsenites, 638
  arseniates, 635
  hydrocyanates, 724
  molybdates, 485
  vegetable bases, salts of, 1152
  antimonites, 497
  antimoniates, 497
  mellitates, 708
  fulminates, 714
  cyanurates, 718
  cyanides, 724
  ferrocyanides, 729
  ferridcyanides, 639
  cobalto-cyanides, 741
  metallo-sulphocyanides, 747
  of melamine, 755
  of ammeline, 756
  urates, 759, 761
  alloxanates, 765
  thionurates, 770
  uramilates, 772
  formobenzoates, 789
  hippurates, 790
  hyposulphobenzoates, 791
Salts, hyposulphobenzidates, 794
  benzilates, 801
  cinnamates, 822
  oxalovinates, 853
  xanthates, 856
  isethionates, 865
  methionate of baryta, 866
  aldehydates, 872
  of oxide of methule, 957
  of amule, 984
  kinates, 1023
  malates, 1119
  citrates, 1003
  tartrates, 1009
  benzoates, 782
  tannates, 994
  gallates, 996
  succinates, 1050
  camphorates, 1027
Santonine, 1119
Saponin, 1122
Saxony blue, 1146
Scale of equivalents, 159, 160
Scheele's green, 459, 639
Scillitine, 1121
Sealing-wax, 1109
Sea water, analysis of, 1242
Sebates, 1056
Seidlitz powders, 1013
Seignette, salt of, 1013
Selenite, 604
Selenium, 267
  its oxide, 267
  sulphuret of, 349
Seleniurets, metallic, 349
  of phosphorus, 349
Semen Cynæ, 1119
Senegine, 1123
Sericates, 1035
Sericine, 1037
Serosity of the blood, 1192
  and serum, 1192
Serum, 1191
Silica, or siliceous earth, 265
Silica, alumina, and iron, mode of analysing compounds of, 1234
Silicates, 266
Silicated alkali, 266
Siliceous waters, analysis of, 1242
Silicium and its compounds, 264
Silico-fluorides, 679
Silicon, 264
  terchloride of, 293
  terbromide of, 316

Silicum liquor, 266
Silver and its compounds, 533
  cyanurate of, 719
  cyanide of, 728
  cobaltocyanide of, 741
  sulphocyanide of, 748
  alloxanate of, 765
  oxalurate of, 769
  fulminating compounds of, 536, 716
  glance, 537
  alloys of, 564
  amalgamation of, 533
  sulphate of, 609
  nitrate of, 620
  phosphates of, 633
  dipyrophosphate of, 634
  arseniates of, 638
  granulated, 537
  horn, 537
Sinnamine, 1156
Sinapoline, 1156
Size, 1193
Slaked lime, 395
Slag formed in the reduction of iron, 425
Smalt, 449
Smilacine, 1122
Soap, 1074
  antimoniated, 1078
Soda, or Natrium, 383
  necessary to the formation of bile, 1216
  tests of, 383
  chloride of, 383
  sulphates of, 603
  sulphite of, 614
  nitrate of, 617
  nitrite of, 621
  perchlorate of, 622
  phosphates of, 629
  pyrophosphates of, 633
  metaphosphates of, 635
  arseniates of, 637
  arsenites of, 638
  borate of, 642
  carbonate of, 647
  oxalate of, 703
  acetate of, 881
  malate of, 1019
  citrates of, 1004
  tartrate of, and potash, 1013
  tartrate of, 1012
Sodium, or Natrium, and its compounds, 382
  chloride of, 383
Sodium, or Natrium,
  hydrosulphuret of, 658
  ferrocyanide of, 734
Solanine, 1165
Solar rays, *vide* Light
Solders, 562
Solids, expansion of, by heat, 24
  liquefaction of, 39
  conducting power of, 12
  specific heat of, 36
Solution, 139
Sorrel, salt of, 702
Spaniolitmine, 1132
Spar, fluor, 319
Specific gravity, 52, 133
  mode of determining, 133
Specific heat, 34
  of gases, 35
Speiss, 452
Spelter, 437
Spermaceti, 1082
  oil, 1082
Spirea ulmaria, volatile oil of, 815
Spirit, proof, 828
  of wine, 828
Spirit of hartshorn, 324
Stannates, 445
Staphysine, 1167
Starch, 920, 1170
  moss or lichen, 1173
Steam, temperature of, 47
  elasticity of, 49
  elastic force of at different temperatures, 1248
  latent heat of, 48
Stearates, 1041
Stearine, 1064
Stearoptene, 1087
Steel, 436
Stramonine, 1165
Stream tin, *vide* Tin
Stibium, 493
Strontia, or Strontites, 392
  tests of, 393
  sulphate of, 604
  sulphite of, 614
  nitrate of, 618
  nitrite of, 621
  carbonate of, 649
  acetate of, 882
Strontianite, 649
Strontium and its compounds, 392
  hydrosulphuret of, 660
  carbo-sulphurets of, 661
Strontium,
  haloid-salts of, 668
Strychnia, 1166
Styracine, 1108
Suboxides, 164
Succinates, 1050
Succinamide, 1049
Succinone, 1050
Suet, *vide* Fat
Sugar, 914
  of lead, 884
  of starch, 919
  of grapes, 919
  of milk, 935
  of diabetes, 919
  compounds of, with bases, 917
  products of decomposition of, 926
  action of acids on, 927
  preparation of, from starch, 220, 920
    from woody fibre, 221, 921
  compounds of, with bases, 923
  mushroom, 942
  tasteless, 942
  action of alkalies on, 929
  action of heat on, 930
  constitution of different kinds of, 933
  remarks on the natural state and formation of different kinds of, 943
Sugar-candy, 914
Sulphate of etherole, 863
Sulphates, 598
  double, 609
Sulphisatyde, 1140
Sulphites, 614
Sulphobenzide, 794
Sulphobenzidates, 794
Sulphocyanurets, 774
Sulphur, 241
  its oxides, 243
  flowers of, 242
  hydrate of, 242
  chlorides of, 290
  bromide of, 315
  compounds of, with carbon, 347
  iodide of, 308
  its attraction for metals, 360
  salts, 568, 657
  bases, 568, 657
  acids, 245, 568, 657

Sulpho-cyanogen, 745
Sulphochlorisatyde, 1140
Sulphamethylane, 963
Sulphovinate of etherole, 861
Sulphonaphthaline and sulphonapthalide, 1180
Sulphurets, metallic, 360
Sulphuret of phosphorus, 348
Sulphuretted hydrogen, 337
Sulphuretted sulphites, 250
Sulphuric ether, 825
Sulphureous and saline waters, 1239
Sun, heat of the, 53
Supporters of combustion, 188
Symbols, 179
Synaptase, 804
Synthesis defined, 6

T.

Tallow, 1081
Tanghinine, 1124
Tannates, 994
Tannin, or Tannic acid, 993
Tantalum, 490
Tantalite, 490
Tartar, 1008
Tartar, boracic, 1813
Tartarized iron, 1016
Tartar, cream of, 1010
    soluble, 1012
    emetic, 1014
Tartralates, 1016
Tartrates, 1009
Taurine, 1201
Teeth, 1197
Telerythrine, 1130
Telescope, construction of, 63
Telluretted hydrogen, 512
Tellurium and its compounds, 510
Temperature, 33
    at which bodies become luminous, 70
    equilibrium of, 10
Tenacity of metals, 353
Test-liquids, their application and their mode of action, 1224
    example of, 1224
Test tube, 1224
Tests for detecting the presence of certain bases and the mode of application, 1228
Tests, effects produced by, on the several substances to which they are applied, 1228
Thebaine, 1162
Thermometer, or thermoscope, 26
Thermometer, Centigrade and Fahrenheit's, table for the conversion of the degrees of one into the other, 1251
    Fahrenheit's, 31
    Reaumur's, 31
    Centigrade, 31
    air, 29
    differential, 29
    formula for converting the expression of one into another, 31
    graduation of, 31
Theobromine, 1169
Thionurates, 770
Thiosinnamine, 1146
Thorina, 410
    its tests, 411
Thorium and its compounds, 410
Tin and its compounds, 442
    alloys of, 562
    oxychlorides of, 672
    permuriate of, 446
Tincal, 642
Titanium and its compounds, 506
Titanofluorides, 680
Tombac, 563
Train oil, 1079
Transfer, galvanic, 117
Treacle, 972
Trona, 647
Trough, galvanic, 101
Tungstates, 489
Tungsten and its compounds, 487
Tungsto-sulphurets, 667
Turkey red, 1116
Turpentine, oil of, 1089
Turpeth mineral, 609
Type, metal for, 563

U.

Ultramarine, 385
Upas poison, 1121
Uramilates, 772
Uramile, 770
Uranium and its compounds, 501
Urates, 759, 761
Urea, 760
    nitrate of, 712
Urethane, 859
Urethylane, 963
Uric oxide, 778
Urine of man, 1203
    analysis of, 1204
    of herbivora, 1205
    of carnivora, 1205
    of serpents, 1205
    importance of, as a manure, 1211
Urinary concretions or calculi, 759, 1203
    cause of, 1214

V.

Vacuum, boiling in, 47
    evaporation in, 50
Vanadium and its compounds, 475
Vaporization, 44
    cause of, 51
Vapour, elastic force of aqueous, at different temperatures, table of, 1248
    dilatation of, 45
    density of, 45
    elasticity of, or tension of, 47
    latent heat of, 48
    presence of, in gases, 53
    table of elastic force of, 47, 1248
    variable quantity in the atmosphere, 54
Vapours of alcohol, ether, oil of turpentine, and petroleum, or naphtha, elastic force of at different temperatures, table of, 1250
Valerates, 1031
Varnishes, resinous, 1110
Varvicite, 420
Vegetable alkalies, 1151
    salts of, 1152
Vegetables, changes that occur during the life, growth, and nutrition of, 1207
    first produce albumen, fibrine, and caseine, 1185
Vegetable tissues, mineral substances essential to, 1207

Vegetation, laws of, 1207, 1212
Veratrine, 1165
Verdigris, 886
Verditter, 651
Vermilion, 533
Vienna green, 886
Vinegar, 874
  theory of making, 875
  qualities of, 876
  from wood, 877
Vinous fermentation, 944
Vision, *vide* Eye, action of
Vital air, *vide* Oxygen
Vitriol, oil of, 245
  blue, 608
  green, 606
  white, 607
Volatile alkali, 693
  bodies, 44
Volta-electric induction, 112
  -electrometer, 113
Volta's pile, 93
Voltaic circles, laws of the action of, 103
  simple, 94
    one described by Davy, 97
  compound, 99
  that of Volta, 100
Volumes, theory of, 171
Volumes, combining, 171
  table of, 172

W.

Water, composition of, 196
Water, rain and snow, rich in oxygen, 1237
Water, spring, well, and river, 1238
  hardness of, the cause of, and how removed, 1237
  properties of, 198
  expansion of, in freezing, 27
  boiling and freezing points of, 31
  of crystallization, 576
Waters, mineral, 1238
  analysis of, 1237
  acidulous, 1238
  alkaline, 1239
  chalybeate, 1239
  sulphureous, 1239
  saline, 1239
  siliceous, 1242
  of the sea, 1241
  of the Dead Sea and River Jordan, 1242
  tables of composition mineral of, 1242, 1244
Watery fusion, 576
Wax, 1084
  Japan, 1085
Welding, 426
White lead, 522, 651
White copper, 517
White precipitate, 696
White vitriol, 607
Wine, oil of, 862, 1032
Witherite, 649
Wood, products of the distillation of, 979
Wood coal, or brown coal, 1175
Woody fibre, 943
  decay of, 1174

X.

Xanthates, 856
Xanthic oxide calculus, 778, 1206
  oil, 856
Xanthopicrine, 1121

Y.

Yeast, 946
Yellow, mineral or patent, 674
  king's, 466
Yellow, chrome, 640
Yellow dyes, 1112
Yttria, 409
Yttrium, 409
Yttro-tantalite, 490

Z.

Zaffre, 448
Zinc and its compounds, 437
  tests of the presence of, 439
  fulminate of, 716
  cyanide of, 726
  ferrocyanide of, 734
  thionurate of, 770
  blende, 437, 440
  brown and blue blaze of, 437
  butter of, 439
  alloys of, 562, 563
  amalgam of, 561
  sulphate of, 607
  acetate of, 883
Zinco-cyanurets, 726
Zinetum, 437
Zirconium and its compounds, 412

THE END.

London:
Printed by S. & J. Bentley, Wilson, and Fley,
Bangor House, Shoe Lane.